

**METAL 8-HYDROXYQUINOLINE-FUNCTIONALIZED POLYMERS  
AND RELATED MATERIALS AND METHODS OF MAKING AND  
USING THE SAME**

**PRIOR RELATED U.S. APPLICATION DATA**

This application claims priority to U.S. patent application serial number  
60/445,701, filed February 6, 2003, and U.S. patent application serial number  
60/500,000 filed September 4, 2003, each of which is incorporated herein by  
reference in its entirety.

**STATEMENT OF GOVERNMENT LICENSE RIGHTS**

The inventors received partial funding support through the Georgia  
Institute of Technology Molecular Design Institute, under prime contract N00014-  
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The Federal Government may retain certain license rights in this invention.

**TECHNICAL FIELD OF THE INVENTION**

This invention relates to the field of electro-optical materials, including  
organic light-emitting diodes (OLEDs) and the emission and electron-transport  
layer of OLEDs.

**BACKGROUND OF THE INVENTION**

Aluminum tris(8-hydroxyquinoline) (Alq<sub>3</sub>) is a very stable and highly  
fluorescent solid-state material, which has utility as the emission and electron-  
transport layer in organic light-emitting diodes (OLEDs). *See, for example:*  
Tang, C. W.; VanSlyke, S. A. *Appl. Phys. Lett.* **1987**, *51*, 913-915; Tang, C. W.;

VanSlyke, S. A.; Chen, C. H. *J. Appl. Phys.* **1989**, *65*, 3610-3616; O'Brien, D. F.; Baldo, M. A.; Thompson, M. E.; Forrest, S. R. *Appl. Phys. Lett.* **1999**, *74*, 442-444; Kido, J.; Hongawa, K.; Okuyama, K.; Nagai, K. *Appl. Phys. Lett.* **1994**, *64*, 815-817; Jang, H.; Do, L.-M.; Kim, Y.; Zyung, T.; Do, Y. *Synth. Met.* **2001**, *121*, 1667-1668, each of which is incorporated herein by reference in its entirety. One of the limitations of using Alq<sub>3</sub> in OLEDs is its limited processability. *See, for example:* Friend, R. H.; Gymer, R. W.; Holmes, A. B.; Burroughes, J. H.; Marks, R. N.; Taliani, C.; Bradley, D. D. C.; Santos, D. A. D.; Bredas, J. L.; Logdlund, M.; Salaneck, W. R. *Nature* **1999**, *397*, 121-128; Chen, C. H.; Shi, J. *Coord. Chem. Rev.* **1998**, *171*, 161-174; each of which is incorporated herein by reference in its entirety. Currently, OLEDs are typically fabricated by solution-processing, yet Alq<sub>3</sub> must typically be vacuum deposited. What are needed are new compounds, materials, compositions, and methods that can address this limited processability problem such that Alq<sub>3</sub> can be more amenable to use in OLEDs.

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## SUMMARY OF THE INVENTION

As disclosed herein, this invention encompasses the synthesis and utility of a polymer-supported metal-(8-hydroxyquinoline) complexes Mq<sub>n</sub> and derivatives and analogs of polymer-supported metal-(8-hydroxyquinoline) complexes Mq<sub>n</sub>, as well as methods of making and using these materials. In one aspect, for example, M is a metal selected from Mg, Zn, Al, Ga, or In; q is independently selected from 8-hydroxyquinoline or a substituted analog thereof, and n depends upon the stoichiometry required by the metal to form a complex of Mg(II), Zn(II), Al(III), Ga(III), or In(III). Thus, in one aspect, throughout this application, Mq<sub>n</sub>-containing monomers or polymers are exemplified for complexes of Alq<sub>3</sub>. Accordingly, Alq<sub>3</sub>-containing monomers or polymers are disclosed as examples of more general monomers containing Mgq<sub>2</sub>, Znq<sub>2</sub>, Alq<sub>3</sub>, Gaq<sub>3</sub>, or Inq<sub>3</sub>; or polymers containing Mgq<sub>2</sub>, Znq<sub>2</sub>, Alq<sub>3</sub>, Gaq<sub>3</sub>, Inq<sub>3</sub>, or combinations thereof.

In one aspect, by combining the fluorescent properties of  $Mq_n$ , such as  $Alq_3$ , with the processability of a polymer, the present invention can address the limited processability problem of  $Alq_3$ , while taking advantage of its stability and its fluorescent properties. Because  $Alq_3$ -functionalized monomers are incorporated into polymers and these  $Alq_3$ -containing polymers can be used in OLEDs, these materials may potentially be fabricated using low-cost manufacturing techniques such as solution-processing and possibly in ink-jet printing. Further these materials may be used more generally as electro-optical materials for a variety of applications.

In one aspect, the present invention provides a synthesis of an  $Mq_n$ -containing or  $Mq_n$ -functionalized compound, including a monomeric compound, wherein the  $Mq_n$ -functionalized compound comprises a polymerizable moiety and an  $Mq_n$ -moiety, and wherein  $q$ , in each instance, comprises an 8-hydroxyquinoline residue,  $M$  is selected from Mg, Zn, Al, Ga, or In, and  $n$  is 2 or 3, depending upon the valence of the metal. In this aspect, the  $Mq_n$ -functionalized compound can further comprise a chemical spacer between the polymerizable moiety and the  $Mq_n$ -moiety, wherein the chemical spacer comprises between 1 and about 30 carbon atoms.

In one aspect, the polymerizable moiety of the  $Mq_n$ -functionalized compound, for example an  $Alq_3$ -functionalized compound, can comprise a cyclic olefin, typically an olefin that is capable of undergoing ring-opening metathesis polymerization (ROMP), although other polymerization methods can also be used. In another aspect, this polymerizable moiety can comprise a strained cyclic olefin. In one aspect, for example, the ROMP of the  $Alq_3$ -containing compound could be completed within about 12 hours under mild polymerization conditions. In yet another aspect, solubility and other properties of the resulting  $Alq_3$ -functionalized polymer were tailored by the incorporation of a co-monomer. This method typically provided co-polymers that retained the optical properties of  $Alq_3$  in solution. While not intending to be bound by theory, this observation indicated

that the polymer coil or backbone of the  $\text{Alq}_3$ -functionalized polymer did not interfere with the luminescence properties of the  $\text{Alq}_3$  pendant group.

In yet another aspect, the present invention provides a method of making an  $\text{Mq}_n$ -functionalized polymer, comprising: preparing a  $q_n$ -functionalized monomer; polymerizing the monomer in the presence or absence of a comonomer to form a  $q_n$ -functionalized polymer; and reacting the polymer with a metal complex to form a  $\text{Mq}_n$ -functionalized polymer.

In another aspect, the present invention provides an  $\text{Mq}_n$ -functionalized compound comprising a polymerizable moiety and an  $\text{Mq}_n$ -moiety, wherein  $q$ , in each instance, comprises an 8-hydroxyquinoline residue,  $M$  is selected from  $\text{Mg}$ ,  $\text{Zn}$ ,  $\text{Al}$ ,  $\text{Ga}$ , or  $\text{In}$ , and  $n$  is 2 or 3, depending upon the valence of the metal. In another aspect, this invention provides an  $\text{Mq}_n$ -functionalized polymer comprising the polymerization product of an  $\text{Mq}_n$ -functionalized monomer. In this aspect, the  $\text{Mq}_n$ -functionalized polymer can comprise the homopolymerization product of an  $\text{Mq}_n$ -functionalized monomer, or the copolymerization product of an  $\text{Mq}_n$ -functionalized monomer and a comonomer. Further, the  $\text{Mq}_n$ -containing monomer can be functionalized with at least one electron-donating group, at least one electron-withdrawing group, or a combination thereof.

In another aspect of this invention, the  $\text{Mq}_n$ -moiety of the monomer or the polymer can be functionalized with at least one electron-donating group, at least one electron-withdrawing group, or a combination thereof. In this aspect, for example, the  $\text{Mq}_n$ -moiety can be functionalized with at least one group independently selected from: a hydrocarbyl group, an oxygen group, a sulfur group, a nitrogen group, a phosphorus group, an arsenic group, a carbon group, a silicon group, a germanium group, a tin group, a lead group, a boron group, an aluminum group, an inorganic group, an organometallic group, or a substituted analog thereof, any one of which having from 1 to about 30 carbon atoms; a halide; hydrogen; or any combination thereof. The inclusion of hydrogen in this list is intended to reflect that the quinoline moiety can optionally be partially saturated.

In another aspect, this invention can encompass a light-emitting diode comprising the polymerization product of the  $Mq_n$ -functionalized monomer.

Another aspect of this invention is a composition comprising the polymerization product of an  $Alq_3$ -functionalized monomer, wherein the  $Alq_3$ -functionalized monomer can comprise a polymerizable moiety and an  $Alq_3$ -moiety, and wherein  $q$ , in each instance, comprises an 8-hydroxyquinoline residue, which, in accordance with this invention, can include a residue of an 8-hydroxyquinoline-like compound, or a functionalized analog of an 8-hydroxyquinoline or an 8-hydroxyquinoline-like compound. In one aspect, for example, the polymerization product of an  $Alq_3$ -functionalized monomer is typically substantially non-crosslinked. Also in this aspect, the  $Alq_3$ -moiety of the  $Alq_3$ -functionalized monomer can be functionalized with at least one electron-donating group, at least one electron-withdrawing group, or a combination thereof.

In yet another aspect, this invention provides a composition that can comprise the polymerization product of at least one  $Alq_3$ -functionalized monomer and at least one comonomer, wherein the  $Alq_3$ -functionalized monomer comprises a polymerizable moiety and an  $Alq_3$ -moiety, and wherein  $q$ , in each instance, comprises an 8-hydroxyquinoline residue, which, in accordance with this invention, can include a residue of an 8-hydroxyquinoline-like compound.

In another aspect, the present invention provides a method of making an  $Alq_3$ -functionalized polymer, comprising:

polymerizing an  $Alq_3$ -functionalized monomer in the presence or absence of at least one comonomer;

wherein the  $Alq_3$ -functionalized monomer comprises a polymerizable moiety and an  $Alq_3$ -moiety; and

wherein  $q$ , in each instance, comprises an 8-hydroxyquinoline residue.

In still another aspect, the present invention provides a method of functionalizing a polymer with an  $Alq_3$  moiety, comprising:

providing an Alq<sub>3</sub>-functionalized monomer; and  
polymerizing an Alq<sub>3</sub>-functionalized monomer in the presence or  
absence of at least one comonomer;

wherein the Alq<sub>3</sub>-functionalized monomer comprises a  
polymerizable moiety and an Alq<sub>3</sub>-moiety; and

wherein q, in each instance, comprises an 8-hydroxyquinoline  
residue.

These and other features, aspects, embodiments, and advantages of the  
present invention will become apparent after a review of the following detailed  
description of the disclosed features.

#### BRIEF DESCRIPTION OF THE FIGURES

FIGURE 1 illustrates the UV/Visible absorption spectra of Alq<sub>3</sub>, the Alq<sub>3</sub>-  
containing monomer 9, and the series of 9:12 copolymers in CHCl<sub>3</sub> solution, as  
described in Table 1.

FIGURE 2 illustrates the emission spectra of Alq<sub>3</sub> and the series of 9:12  
copolymers in CHCl<sub>3</sub> solution, excited at 380 nm, as described in Table 1.

FIGURE 3 provides examples of modified 8-hydroxyquinoline ligands  
used in the preparation of functionalized Alq<sub>3</sub>-containing monomers and Alq<sub>3</sub>-  
containing polymers.

FIGURE 4 provides normalized solution emission spectra of selected  
modified polymers in chloroform.

FIGURE 5 provides solid-state emission spectra of selected modified  
polymers on quartz.

FIGURE 6 provides solid-state emission spectra of three different  
comonomer ratios of the Alq<sub>3</sub>-polymer.

FIGURE 7 provides solid-state emission spectra of three different  
comonomer ratios of the CHO-polymer.

FIGURE 8 provides solid-state emission spectra of 3 different comonomer  
ratios of the PVK-polymer.

FIGURE 9 provides examples of catalysts that can be used for polymerizing the functionalized monomers to the functionalized polymers, based on a ring-opening metathesis polymerization (ROMP) catalytic process.

FIGURE 10 illustrates the solution fluorescence spectra (normalized intensity vs. wavelength (nm)) of all Znq<sub>2</sub>-functionalized copolymers, excited at 380 nm, except for the **Naph** copolymer which was excited at 330 nm.

FIGURE 11 demonstrates that the emission (normalized intensity vs. wavelength (nm)) of the Znq<sub>2</sub>-functionalized copolymers can be tuned solid-state from blue (427 nm) to the yellow (565 nm) through modifications on the second functionalized quinoline.

## DETAILED DESCRIPTION OF THE INVENTION

The present invention addresses some of the current limitations in using Alq<sub>3</sub> and related Mq<sub>n</sub> compounds in electro-optical materials, including OLEDs, such as its limited processability, by providing a series of Mq<sub>n</sub>-containing monomers, which comprise a polymerizable moiety and an Mq<sub>n</sub>-moiety which can be functionalized, and by providing an Mq<sub>n</sub>-containing polymer comprising the polymerization product of an Mq<sub>n</sub>-functionalized monomer. Further, the Mq<sub>n</sub>-containing polymer can comprise the homopolymerization product of an Mq<sub>n</sub>-functionalized monomer, or the copolymerization product of an Mq<sub>n</sub>-functionalized monomer and a comonomer, in which the comonomer and the polymerization conditions, including the ratio of comonomer to Mq<sub>n</sub>-containing monomer, may be used to tailor the properties of the resulting polymer. This invention further encompasses a light-emitting diode comprising a Mq<sub>n</sub>-functionalized polymer.

Thus, in one aspect, for example, this invention provides Mq<sub>n</sub>-containing polymers, where the Mq<sub>n</sub> complex is embedded within a polymer matrix. In this aspect, the Mq<sub>n</sub>, such as Alq<sub>3</sub>, is typically covalently attached to the polymer backbone, which can be accomplished by covalently attaching the Mq<sub>n</sub> moiety to the polymerizable monomer, prior to its polymerization. By providing a fully-

functionalized monomer that can be polymerized in a controlled fashion, this process substantially eliminates any crosslinking, and hence provides a fully-functionalized polymer without substantial crosslinking. Additionally, the polymer structure can be controlled and altered by using co-monomers to tune the polymeric properties.

#### Preparation of $Mq_n$ -Functionalized Monomers

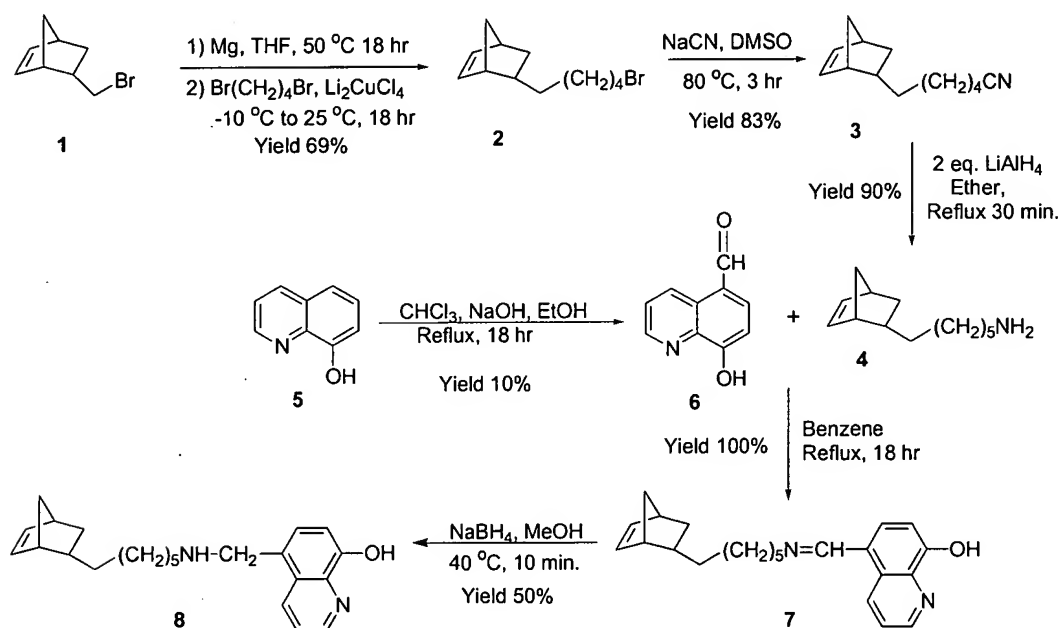
In one aspect the  $Mq_n$ -containing monomer typically includes two structural motifs: 1) a polymerizable unit or moiety that provides the required degree of control during the polymerization process; and 2) an  $Mq_n$ -moiety or residue, which typically comprises Mg(II), Zn(II), Al(III), Ga(III), or In(III) coordinated with two or three, independently selected, 8-hydroxyquinoline-type residues, as disclosed herein. The term 8-hydroxyquinoline residue is used to refer to, among other things, an 8-hydroxyquinoline ligand that can be functionalized with at least one electron-donating group, at least one electron-withdrawing group, or a combination thereof; can be deprotonated; or can be not functionalized; and the like; or any combination of these. This term is also used to refer to 8-hydroxyquinoline-like ligands such as, for example, ligands in which either another heteroatom is present in one of the 6-membered rings of the 8-hydroxyquinoline ligand, or a partially hydrogenated 8-hydroxyquinoline-like ligand. Further, the  $Mq_n$ -containing monomer typically includes a third, optional, structural motif, namely: 3) an alkyl spacer between the polymerizable unit and the  $Mq_n$  to decouple the backbone from the  $Mq_n$  group.

In one aspect, norbornene could be as the polymerizable unit. Norbornene can be polymerized using ring-opening metathesis polymerization (ROMP), a method that has a high tolerance to many functional groups. *See, for example:* Fürstner, A. *Angew. Chem. Int. Ed.* **2000**, 39, 3012-3043; Piotti, M. E. *Curr. Opin. Solid State Mater. Sci.* **1999**, 4, 539-547; Bielawski, C. W.; Grubbs, R. H. *Angew. Chem. Int. Ed.* **2000**, 39, 2903-2906; and Sanford, M. S.; Ulman, M.; Grubbs, R. H. *J. Am. Chem. Soc.* **2001**, 123, 749-750; each of which is



incorporated herein by reference, in its entirety. Furthermore, ROMP is often a living polymerization method resulting in polymers with controlled molecular weights, low polydispersities, and also allows for the formation of block co-polymers. See also, for example: Ivin, K. J. *Olefin Metathesis* Academic Press: London, 1996; Ivin, K. J. and Mol, J. C. *Olefin Metathesis and Metathesis Polymerization* Academic Press: New York, 1997; each of which is incorporated herein by reference, in its entirety.

Scheme 1



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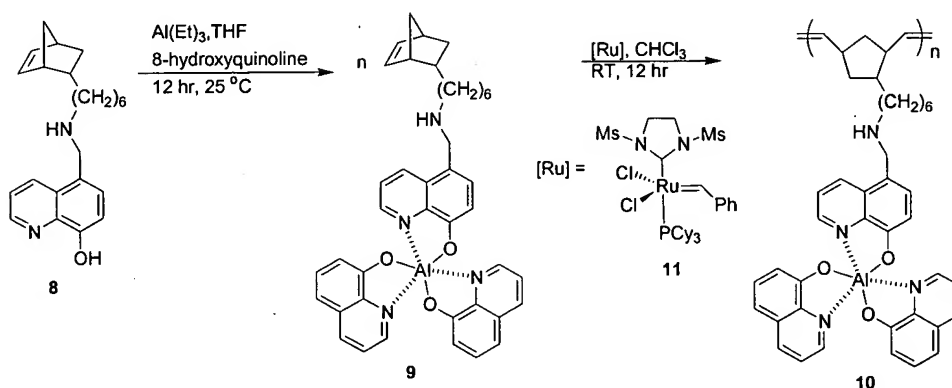
In one aspect, for example, the synthesis of a  $\text{Mq}_n$ -containing monomer encompasses the synthesis of a metal-free monomer as presented in Scheme 1, followed by metallating the monomer. As presented in Scheme 1 and in the Examples, this reaction sequence began with the functionalization of norbornene to form bromomethyl norbornene 1, formed using a Diels-Alder reaction between allyl bromide and cyclopentadiene. Attachment of a bromoalkyl chain using Grignard chemistry, followed by the conversion of the bromide to the nitrile and subsequent reduction of the nitrile, resulted in the precursor 4 in an overall yield

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of 51%. Compound **4** was then coupled to **6**, itself prepared from compound **5** (8-hydroxyquinoline) as shown, followed by the reduction of the resulting imine to yield monomer **8**. (See: Clemo, G. R.; Howe, R. *J. Chem. Soc.* **1955**, 3552-3553; which is incorporated herein by reference in its entirety.)

As illustrated in Scheme 2, the formation of the  $Mq_n$ -functionalized monomer, such as the  $Alq_3$ -functionalized monomer **9** was achieved, for example, by adding monomer **8** to ten equivalents of triethylaluminum, followed by twenty equivalents of 8-hydroxyquinoline. This reaction resulted in the formation of one equivalent of **9** and nine equivalents of non-functionalized  $Alq_3$ . In one aspect, this procedure was developed to substantially achieve full metallation of each monomer without coordination of two monomer units onto the same aluminum center, thereby substantially preventing any cross-linking during the polymerization. The statistical probability of having two monomer units attached to the same aluminum center is 0.1%. While this number is negligible and no cross-linking was observed, a very small amount of cross-linking at this point could not be excluded.

Scheme 2



Thus, in one aspect, this invention provides an  $Mq_n$ -functionalized compound comprising a polymerizable moiety and an  $Mq_n$ -moiety, wherein  $q$ , in each instance, comprises an 8-hydroxyquinoline residue, and  $M$  is selected from

Mg, Zn, Al, Ga, or In; and  $n$  is selected from 2 or 3, as the stoichiometry of the complex dictates based upon the valence of the metal.

In another aspect, this invention provides an  $Alq_3$ -functionalized compound comprising a polymerizable moiety and an  $Alq_3$ -moiety, wherein  $q$ , in  
5 each instance, comprises an 8-hydroxyquinoline residue. In this aspect, the  $Alq_3$ -moiety can be functionalized with at least one electron-donating group, at least one electron-withdrawing group, or a combination thereof, which can be used to tune the optical properties of the  $Alq_3$ -functionalized compounds, monomers, and polymers. Thus, it is known that the usual blue-green luminescence of  $Alq_3$  can  
10 be either blue- or red-shifted through the addition of substituents to the 8-hydroxyquinoline residue.

In another aspect, the  $Mq_n$ -functionalized monomer can further comprise a chemical spacer between the polymerizable moiety and the  $Mq_n$ -moiety, and the chemical spacer can optionally be functionalized with at least one electron-  
15 donating group, at least one electron-withdrawing group, or a combination thereof. Thus, in one aspect, the chemical spacer comprises an alkyl linkage or spacer group, having between 1 and about 30 carbon atoms. In another aspect, the chemical spacer comprises an alkyl linkage or spacer group, having greater than or equal to about 4 carbon atoms. While not intending to be bound by  
20 theory, it is believed that this spacer was employed to assist in decoupling the motion of the backbone from the pendant  $Mq_n$ -group.

Also in this aspect, for example, the  $Mq_n$ -moiety can be functionalized with at least one group independently selected from: a hydrocarbyl group, an oxygen group, a sulfur group, a nitrogen group, a phosphorus group, an arsenic  
25 group, a carbon group, a silicon group, a germanium group, a tin group, a lead group, a boron group, an aluminum group, an inorganic group, an organometallic group, or a substituted analog thereof, any one of which having from 1 to about 30 carbon atoms; a halide; hydrogen; or any combination thereof, as long as these groups do not terminate the fluorescent properties of the resulting monomer and  
30 the resulting polymer. This list of possible substituents includes hydrogen,

therefore the notion of a partially saturated analog or derivative of 8-hydroxyquinoline is encompassed by this invention. Further the substituents are independently selected, therefore, examples of these groups are provided below which are selected in each instance they appear in the functionalized Alq<sub>3</sub>-moiety, as long as these groups do not terminate the fluorescent properties of the resulting monomer and the resulting polymer.

Examples of each of these substituent groups include, but are not limited to, the following groups. In each example presented below, unless otherwise specified, R is independently selected from a hydrocarbyl group, including, but not limited to, an aliphatic group; an aromatic group; a cyclic group; any combination thereof; any substituted derivative thereof, including but not limited to, a halide-, an alkoxide-, or an amide-substituted derivative thereof; any one of which has from 1 to about 30 carbon atoms; or hydrogen. Also included in these groups are any unsubstituted, branched, or linear analogs thereof.

Examples of hydrocarbyl groups include aliphatic groups which, in each instance, include, but are not limited to, an alkyl group, a cycloalkyl group, an alkenyl group, a cycloalkenyl group, an alkynyl group, an alkadienyl group, a cyclic group, and the like, and includes all substituted, unsubstituted, branched, and linear analogs or derivatives thereof, in each instance having from one to about 30 carbon atoms. Thus, aliphatic groups include, but are not limited to, hydrocarbyls such as paraffins and alkenyls. For example, aliphatic groups as used herein include methyl, ethyl, propyl, n-butyl, tert-butyl, sec-butyl, isobutyl, amyl, isoamyl, hexyl, cyclohexyl, heptyl, octyl, nonyl, decyl, dodecyl, 2-ethylhexyl, pentenyl, butenyl, and the like.

Examples of hydrocarbyl groups also include aromatic groups which, in each instance, include, but are not limited to, phenyl, naphthyl, anthracenyl, and the like, including substituted derivatives thereof, in each instance having from 6 to about 30 carbons. Substituted derivatives of aromatic compounds include, but are not limited to, tolyl, xylyl, mesityl, and the like, including any heteroatom substituted derivative thereof.

Examples of hydrocarbonyl groups further include cyclic organic groups which, in each instance, include, but are not limited to, cycloparaffins, cycloolefins, cycloacetylenes, arenes such as phenyl, bicyclic groups and the like, including substituted derivatives thereof, in each instance having from about 3 to  
5 about 30 carbon atoms. Thus heteroatom-substituted cyclic groups such as furanyl are included herein.

In each instance, hydrocarbonyl groups further include groups that contain both aliphatic and cyclic portions, examples of which include, but are not limited to, groups such as:  $-(CH_2)_mC_6H_qR_{5-q}$  wherein m is an integer from 1 to about 10,  
10 q is an integer from 1 to 5, inclusive;  $(CH_2)_mC_6H_qR_{10-q}$  wherein m is an integer from 1 to about 10, q is an integer from 1 to 10, inclusive; and  $(CH_2)_mC_5H_qR_{9-q}$  wherein m is an integer from 1 to about 10, q is an integer from 1 to 9, inclusive. In each instance and as defined above, R is independently selected from: an aliphatic group; an aromatic group; a cyclic group; any combination thereof; any  
15 substituted derivative thereof, including but not limited to, a halide-, an alkoxide-, or an amide-substituted derivative thereof; any one of which has from 1 to about 30 carbon atoms; or hydrogen. In one aspect, aliphatic and cyclic groups include, but are not limited to:  $-CH_2C_6H_5$ ;  $-CH_2C_6H_4F$ ;  $-CH_2C_6H_4Cl$ ;  $-CH_2C_6H_4Br$ ;  $-CH_2C_6H_4I$ ;  $-CH_2C_6H_4OMe$ ;  $-CH_2C_6H_4OEt$ ;  $-CH_2C_6H_4NH_2$ ;  $-CH_2C_6H_4NMe_2$ ;  $-CH_2C_6H_4NEt_2$ ;  
20  $-CH_2CH_2C_6H_5$ ;  $-CH_2CH_2C_6H_4F$ ;  $-CH_2CH_2C_6H_4Cl$ ;  $-CH_2CH_2C_6H_4Br$ ;  $-CH_2CH_2C_6H_4I$ ;  $-CH_2CH_2C_6H_4OMe$ ;  $-CH_2CH_2C_6H_4OEt$ ;  $-CH_2CH_2C_6H_4NH_2$ ;  $-CH_2CH_2C_6H_4NMe_2$ ;  $-CH_2CH_2C_6H_4NEt_2$ ; any regioisomer thereof, and any substituted derivative thereof.

Examples of halides, in each instance, include fluoride, chloride, bromide,  
25 and iodide.

In each instance, oxygen groups are oxygen-containing groups, examples of which include, but are not limited to, alkoxy or aryloxy groups ( $-OR$ ),  $-OC(O)R$ ,  $-OC(O)H$ ,  $-OSiR_3$ ,  $-OPR_2$ ,  $-OAlR_2$ , and the like, including substituted derivatives thereof, wherein R in each instance is selected from alkyl, cycloalkyl,  
30 aryl, aralkyl, substituted alkyl, substituted aryl, or substituted aralkyl having from

1 to about 30 carbon atoms. Examples of alkoxy or aryloxy groups (-OR) groups include, but are not limited to, methoxy, ethoxy, propoxy, butoxy, phenoxy, substituted phenoxy, and the like.

5 In each instance, sulfur groups are sulfur-containing groups, examples of which include, but are not limited to, -SR, -OSO<sub>2</sub>R, -OSO<sub>2</sub>OR, -SCN, -SO<sub>2</sub>R, and the like, including substituted derivatives thereof, wherein R in each instance is selected from alkyl, cycloalkyl, aryl, aralkyl, substituted alkyl, substituted aryl, or substituted aralkyl having from 1 to about 30 carbon atoms.

10 In each instance, nitrogen groups are nitrogen-containing groups, which include, but are not limited to, -NH<sub>2</sub>, -NHR, -NR<sub>2</sub>, -NO<sub>2</sub>, -N<sub>3</sub>, and the like, including substituted derivatives thereof, wherein R in each instance is selected from alkyl, cycloalkyl, aryl, aralkyl, substituted alkyl, substituted aryl, or substituted aralkyl having from 1 to about 30 carbon atoms.

15 In each instance, phosphorus groups are phosphorus-containing groups, which include, but are not limited to, -PH<sub>2</sub>, -PHR, -PR<sub>2</sub>, -P(O)R<sub>2</sub>, -P(OR)<sub>2</sub>, -P(O)(OR)<sub>2</sub>, and the like, including substituted derivatives thereof, wherein R in each instance is selected from alkyl, cycloalkyl, aryl, aralkyl, substituted alkyl, substituted aryl, or substituted aralkyl having from 1 to about 30 carbon atoms.

20 In each instance, arsenic groups are arsenic-containing groups, which include, but are not limited to, -AsHR, -AsR<sub>2</sub>, -As(O)R<sub>2</sub>, -As(OR)<sub>2</sub>, -As(O)(OR)<sub>2</sub>, and the like, including substituted derivatives thereof, wherein R in each instance is selected from alkyl, cycloalkyl, aryl, aralkyl, substituted alkyl, substituted aryl, or substituted aralkyl having from 1 to about 30 carbon atoms.

25 In each instance, carbon groups are carbon-containing groups, which include, but are not limited to, alkyl halide groups that comprise halide-substituted alkyl groups with 1 to about 30 carbon atoms, aralkyl groups with 1 to about 30 carbon atoms, -C(O)H, -C(O)R, -C(O)OR, cyano, -C(NR)H, -C(NR)R, -C(NR)OR, and the like, including substituted derivatives thereof, wherein R in each instance is selected from alkyl, cycloalkyl, aryl, aralkyl, substituted alkyl,  
30 substituted aryl, or substituted aralkyl having from 1 to about 30 carbon atoms.

In each instance, silicon groups are silicon-containing groups, which include, but are not limited to, silyl groups such alkylsilyl groups, arylsilyl groups, arylalkylsilyl groups, siloxy groups, and the like, which in each instance have from 1 to about 30 carbon atoms. For example, silicon groups include  
5 trimethylsilyl and phenyloctylsilyl groups.

In each instance, germanium groups are germanium-containing groups, which include, but are not limited to, germyl groups such alkylgermyl groups, arylgermyl groups, arylalkylgermyl groups, germyloxy groups, and the like, which in each instance have from 1 to about 30 carbon atoms.

10 In each instance, tin groups are tin-containing groups, which include, but are not limited to, stannyl groups such alkylstannyl groups, arylstannyl groups, arylalkylstannyl groups, stanoxo groups, and the like, which in each instance have from 1 to about 30 carbon atoms. Thus, tin groups include, but are not limited to, stanoxo groups.

15 In each instance, lead groups are lead-containing groups, which include, but are not limited to, alkyllead groups, aryllead groups, arylalkyllead groups, and the like, which in each instance, have from 1 to about 30 carbon atoms.

In each instance, boron groups are boron-containing groups, which include, but are not limited to,  $-BR_2$ ,  $-BX_2$ ,  $-BRX$ , wherein X is a monoanionic group such as halide, hydride, alkoxide, alkyl thiolate, and the like, and wherein R  
20 in each instance is selected from alkyl, cycloalkyl, aryl, aralkyl, substituted alkyl, substituted aryl, or substituted aralkyl having from 1 to about 30 carbon atoms.

In each instance, aluminum groups are aluminum-containing groups, which include, but are not limited to,  $-AlR_2$ ,  $-AlX_2$ ,  $-AlRX$ , wherein X is a  
25 monoanionic group such as halide, hydride, alkoxide, alkyl thiolate, and the like, and wherein R in each instance is selected from alkyl, cycloalkyl, aryl, aralkyl, substituted alkyl, substituted aryl, or substituted aralkyl having from 1 to about 30 carbon atoms.

30 Examples of inorganic groups that may be used as substituents for substituted cyclopentadienyls, substituted indenyls, substituted fluorenyls, and

substituted boratabenzenes, in each instance, include, but are not limited to, -SO<sub>2</sub>X, -OAlX<sub>2</sub>, -OSiX<sub>3</sub>, -OPX<sub>2</sub>, -SX, -OSO<sub>2</sub>X, -AsX<sub>2</sub>, -As(O)X<sub>2</sub>, -PX<sub>2</sub>, and the like, wherein X is a monoanionic group such as halide, hydride, amide, alkoxide, alkyl thiolate, and the like, and wherein any alkyl, cycloalkyl, aryl, aralkyl, substituted alkyl, substituted aryl, or substituted aralkyl group or substituent on these ligands has from 1 to about 30 carbon atoms.

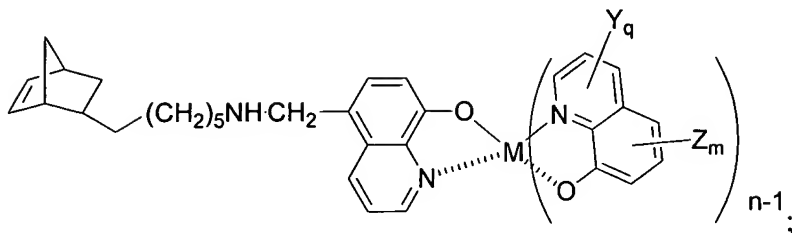
Examples of organometallic groups that may be used as substituents for substituted cyclopentadienyls, substituted indenyls, and substituted fluorenyls, in each instance, include, but are not limited to, organoboron groups, organoaluminum groups, organogallium groups, organosilicon groups, organogermanium groups, organotin groups, organolead groups, organo-transition metal groups, and the like, having from 1 to about 30 carbon atoms.

In another aspect, this invention provides an Mq<sub>n</sub>-functionalized compound comprising a polymerizable moiety and an Mq<sub>n</sub>-moiety, wherein q, in each instance, comprises an 8-hydroxyquinoline residue, and M is selected from Mg, Zn, Al, Ga, or In; and n is selected from 2 or 3, depending upon the valence of the metal. The Mq<sub>n</sub>-moiety can be functionalized with at least one electron-donating group, at least one electron-withdrawing group, or a combination thereof. In yet another aspect, Mq<sub>n</sub>-moiety can be functionalized with at least one group independently selected from: a hydrocarbyl group, an oxygen group, a sulfur group, a nitrogen group, a phosphorus group, an arsenic group, a carbon group, a silicon group, a germanium group, a tin group, a lead group, a boron group, an aluminum group, an inorganic group, an organometallic group, or a substituted analog thereof, any one of which having from 1 to about 30 carbon atoms; a halide; hydrogen; or any combination thereof.

In still another aspect, this invention provides an Mq<sub>n</sub>-functionalized compound comprising a polymerizable moiety and an Mq<sub>n</sub>-moiety, wherein q, in each instance, comprises an 8-hydroxyquinoline residue, and M is selected from Mg, Zn, Al, Ga, or In; and n is selected from 2 or 3 according to the valence of



the metal, wherein the compound has the formula



wherein Y and Z are independently selected from -F, -Cl, -Br, -I, -R<sup>1</sup>, -CR<sup>1</sup>=O, -CH=CHC(O)R<sup>1</sup>, -C(O)R<sup>1</sup>, -C(O)OR<sup>1</sup>, -CN, -C(NR<sup>1</sup>)R<sup>1</sup>, -C(NR<sup>1</sup>)OR<sup>1</sup>, -CH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>X, -CH<sub>2</sub>C<sub>6</sub>H<sub>3</sub>X<sub>2</sub>, -CH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>R<sup>1</sup>, -CH<sub>2</sub>C<sub>6</sub>H<sub>3</sub>R<sup>1</sup><sub>2</sub>, -CH<sub>2</sub>CH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>X, -CH<sub>2</sub>CH<sub>2</sub>C<sub>6</sub>H<sub>3</sub>X<sub>2</sub>, CH<sub>2</sub>CH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>R<sup>1</sup>, -CH<sub>2</sub>CH<sub>2</sub>C<sub>6</sub>H<sub>3</sub>R<sup>1</sup><sub>2</sub>, -CH=CR<sup>1</sup><sub>2</sub>, -C≡CR<sup>1</sup>, -OR<sup>1</sup>, -OC(O)R<sup>1</sup>, -SiR<sup>1</sup><sub>3</sub>, -OSiR<sup>1</sup><sub>3</sub>, -NO<sub>2</sub>, -NR<sup>1</sup><sub>2</sub>, -N<sub>3</sub>, -N=CR<sup>1</sup><sub>2</sub>, -N=NR<sup>1</sup>, -SR<sup>1</sup>, -SX, -OSO<sub>2</sub>R<sup>1</sup>, -OSO<sub>2</sub>OR<sup>1</sup>, -SCN, -SO<sub>2</sub>R<sup>1</sup>, -PR<sup>1</sup><sub>2</sub>, -PX<sub>2</sub>, -P(O)R<sup>1</sup><sub>2</sub>, -P(OR<sup>1</sup>)<sub>2</sub>, -P(O)(OR<sup>1</sup>)<sub>2</sub>, -OSiR<sup>1</sup><sub>3</sub>, -OPR<sup>1</sup><sub>2</sub>, -OAlR<sup>1</sup><sub>2</sub>, -AsR<sup>1</sup><sub>2</sub>, -As(O)R<sup>1</sup><sub>2</sub>, -As(OR<sup>1</sup>)<sub>2</sub>, -As(O)(OR<sup>1</sup>)<sub>2</sub>, SnR<sup>1</sup><sub>3</sub>, OSnR<sup>1</sup><sub>3</sub>, SnX<sup>1</sup><sub>3</sub>, OSnX<sup>1</sup><sub>3</sub>, -BR<sup>1</sup><sub>2</sub>, -BX<sub>2</sub>, -BR<sup>1</sup>X, -SO<sub>2</sub>X, -OAlX<sub>2</sub>, -OSiX<sub>3</sub>, -OPX<sub>2</sub>, -OSO<sub>2</sub>X, -AsX<sub>2</sub>, or -As(O)X<sub>2</sub>;

wherein R<sup>1</sup>, in each instance, is independently selected from H or a substituted or unsubstituted hydrocarbyl group having from 1 to about 30 carbon atoms;

wherein X, in each instance, is independently selected from F, Cl, Br, I, H, OR<sup>1</sup>, -SR<sup>1</sup>, or NR<sup>1</sup><sub>2</sub>; and

wherein q and m are independently selected from an integer from 0 to 3.

The present invention further encompasses a method of making a Mq<sub>n</sub>-functionalized polymer, comprising:

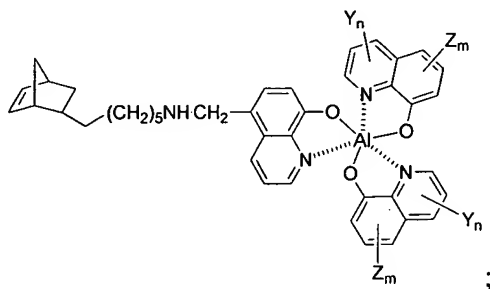
preparing a q<sub>n</sub>-functionalized monomer;

polymerizing the monomer in the presence or absence of a comonomer to form a q<sub>n</sub>-functionalized polymer; and

reacting the polymer with a metal complex to form a Mq<sub>n</sub>-functionalized polymer;

wherein M is selected from Mg, Zn, Al, Ga, or In; and n is selected from 2 or 3, depending upon the valence of the metal. In another aspect, M is selected from Zn or Al.

In another aspect, this invention provides an Alq<sub>3</sub>-functionalized compound wherein the compound has the following formula:



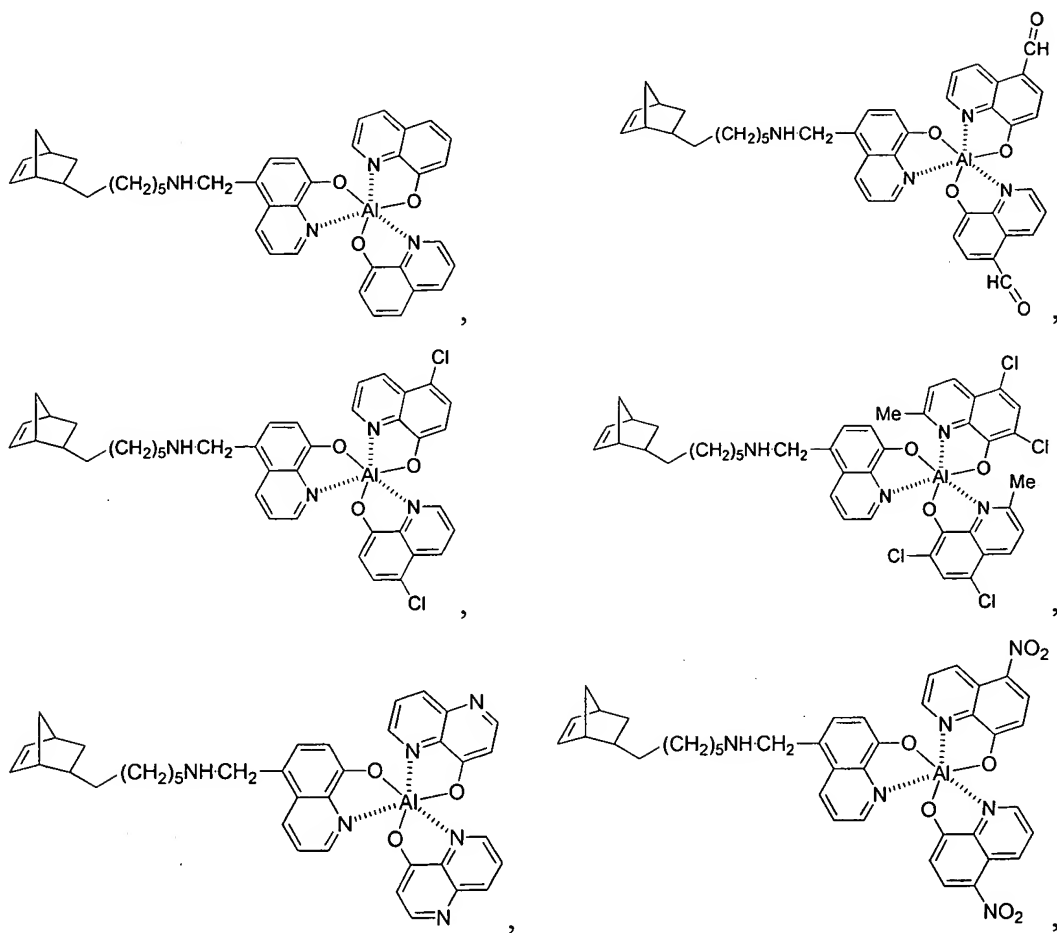
wherein Y and Z are independently selected from -F, -Cl, -Br, -I, -R<sup>1</sup>, -CR<sup>1</sup>=O, -CH=CHC(O)R<sup>1</sup>, -C(O)R<sup>1</sup>, -C(O)OR<sup>1</sup>, -CN, -C(NR<sup>1</sup>)R<sup>1</sup>, -C(NR<sup>1</sup>)OR<sup>1</sup>, -CH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>X, -CH<sub>2</sub>C<sub>6</sub>H<sub>3</sub>X<sub>2</sub>, -CH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>R<sup>1</sup>, -CH<sub>2</sub>C<sub>6</sub>H<sub>3</sub>R<sup>1</sup><sub>2</sub>, -CH<sub>2</sub>CH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>X, -CH<sub>2</sub>CH<sub>2</sub>C<sub>6</sub>H<sub>3</sub>X<sub>2</sub>, CH<sub>2</sub>CH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>R<sup>1</sup>, -CH<sub>2</sub>CH<sub>2</sub>C<sub>6</sub>H<sub>3</sub>R<sup>1</sup><sub>2</sub>, -CH=CR<sup>1</sup><sub>2</sub>, -C≡CR<sup>1</sup>, -OR<sup>1</sup>, -OC(O)R<sup>1</sup>, -SiR<sup>1</sup><sub>3</sub>, -OSiR<sup>1</sup><sub>3</sub>, -NO<sub>2</sub>, -NR<sup>1</sup><sub>2</sub>, -N<sub>3</sub>, -N=CR<sup>1</sup><sub>2</sub>, -N=NR<sup>1</sup>, -SR<sup>1</sup>, -SX, -OSO<sub>2</sub>R<sup>1</sup>, -OSO<sub>2</sub>OR<sup>1</sup>, -SCN, -SO<sub>2</sub>R<sup>1</sup>, -PR<sup>1</sup><sub>2</sub>, -PX<sub>2</sub>, -P(O)R<sup>1</sup><sub>2</sub>, -P(OR<sup>1</sup>)<sub>2</sub>, -P(O)(OR<sup>1</sup>)<sub>2</sub>, -OSiR<sup>1</sup><sub>3</sub>, -OPR<sup>1</sup><sub>2</sub>, -OAlR<sup>1</sup><sub>2</sub>, -AsR<sup>1</sup><sub>2</sub>, -As(O)R<sup>1</sup><sub>2</sub>, -As(OR<sup>1</sup>)<sub>2</sub>, -As(O)(OR<sup>1</sup>)<sub>2</sub>, SnR<sup>1</sup><sub>3</sub>, OSnR<sup>1</sup><sub>3</sub>, SnX<sup>1</sup><sub>3</sub>, OSnX<sup>1</sup><sub>3</sub>, -BR<sup>1</sup><sub>2</sub>, -BX<sub>2</sub>, -BR<sup>1</sup>X, -SO<sub>2</sub>X, -OAlX<sub>2</sub>, -OSiX<sub>3</sub>, -OPX<sub>2</sub>, -OSO<sub>2</sub>X, -AsX<sub>2</sub>, or -As(O)X<sub>2</sub>;

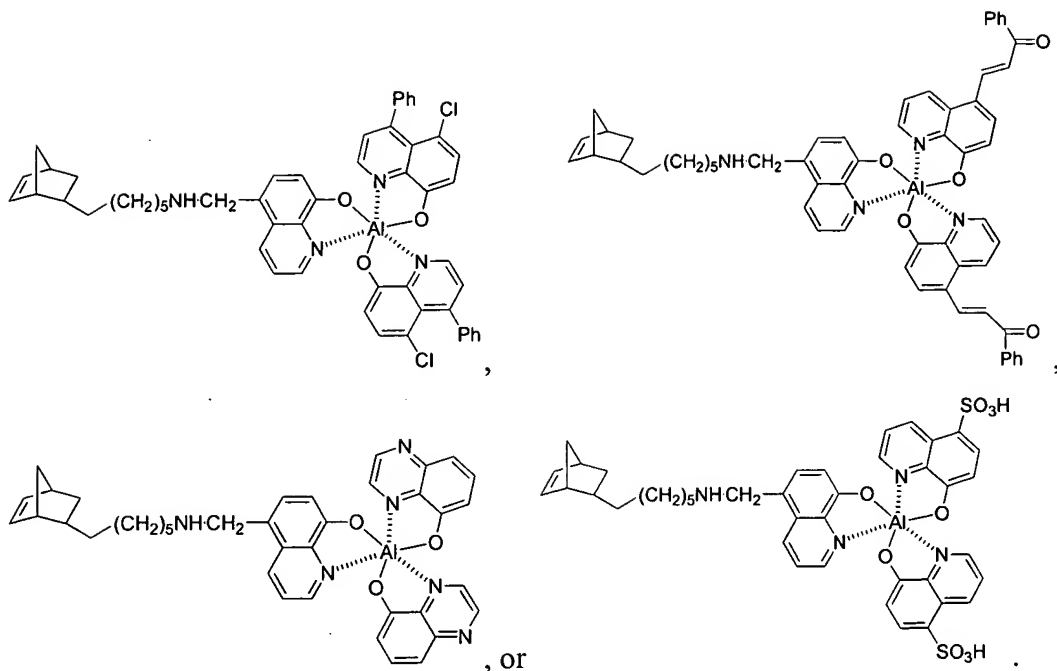
wherein R<sup>1</sup>, in each instance, is independently selected from H or a substituted or unsubstituted hydrocarbonyl group having from 1 to about 30 carbon atoms;

wherein X, in each instance, is independently selected from F, Cl, Br, I, H, OR<sup>1</sup>, -SR<sup>1</sup>, or NR<sup>1</sup><sub>2</sub>; and

wherein n and m are independently selected from an integer from 0 to 3. Thus, this list of possible substituents includes hydrogen, therefore the notion of a partially saturated analog or derivative of 8-hydroxyquinoline is encompassed by this invention.

In yet another aspect, the present invention provides an Alq<sub>3</sub>-functionalized compound including, but not limited to:





In yet another aspect, the present invention provides an  $Mq_n$ -functionalized compound comprising a polymerizable moiety and an  $Mq_n$ -moiety, wherein the polymerizable moiety comprises norbornene, norbornadiene, cyclopentene, cyclooctene, cyclooctadiene, or a functionalized analog thereof. In yet another aspect, the polymerizable moiety comprises norbornene.

In still another aspect, the present invention provides an  $Mq_n$ -functionalized compound comprising a polymerizable moiety and an  $Mq_n$ -moiety, which further comprises a chemical spacer between the polymerizable moiety and the  $Mq_n$ -moiety, having between 1 and about 30 carbon atoms. In this aspect, for example, the chemical spacer is selected from  $-(CH_2)_nNR^1CH_2-$ , wherein  $n$  in the formula of the spacer is from 1 to about 12, and  $R^1$  is selected from H or a hydrocarbyl or substituted hydrocarbyl having from 1 to about 30 carbon atoms. Thus, the chemical spacer can be  $-(CH_2)_nNHCH_2-$ .

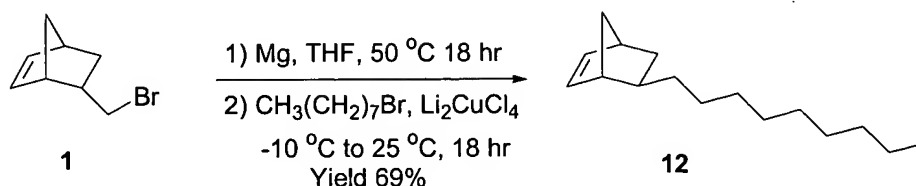
In still another aspect, this invention provides a light-emitting diode comprising the polymerization product of any  $Mq_n$ -functionalized compound disclosed herein.

### Preparation of $Mq_n$ -Functionalized Homo- and CoPolymers

The formation of the  $Alq_3$ -functionalized monomer **9** was achieved, for example, by adding monomer **8** to ten equivalents of triethylaluminum, followed by twenty equivalents of 8-hydroxyquinoline, as illustrated in Scheme 2 and in the Examples provided herein. This reaction resulted in the formation of one equivalent of **9** and nine equivalents of non-functionalized  $Alq_3$ . This 9:1 mixture ( $Alq_3$ :**9**) could be used directly in the polymerizations, which were carried out in chloroform at room temperature using the ruthenium catalyst **11**. Under these conditions, a 50:1 monomer to catalyst ratio was fully polymerized to polymer **10** within 12 hours. After complete polymerization, the excess  $Alq_3$  was removed from the polymer through extensive washings with methanol and methylene chloride, yielding a polymer without any impurities. The formation of the  $Znq_2$ -functionalized monomer was achieved similarly, using  $ZnEt_2$  in place of  $AlEt_3$  in Scheme 2.

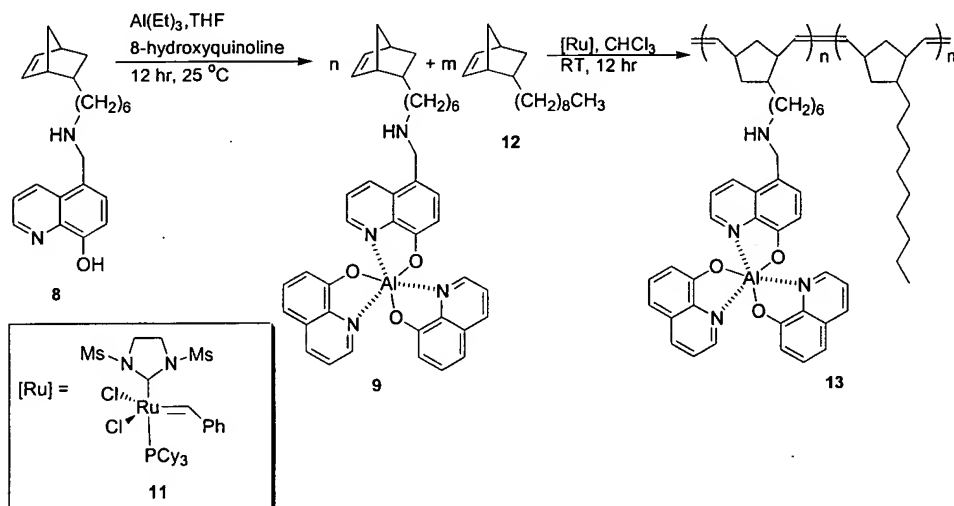
The formation of the other  $Mq_n$ -functionalized monomers, wherein  $Mq_n$  is selected from  $Mgq_2$ ,  $Gaq_3$ , or  $Inq_3$ , may be achieved in a similar manner as that disclosed in Scheme 2, for example, by adding monomer **8** to an excess (about 10 equivalents) of metal halides, including, but not limited to,  $MgCl_2$ ,  $GaCl_3$ , or  $InCl_3$ , respectively, followed by an excess (about twenty equivalents) of 8-hydroxyquinoline. Other halides such as bromides and iodides may be used as well. These  $Mq_n$ -functionalized monomers may then be polymerized as indicated in Scheme 2.

Scheme 3



Solubility of the Alq<sub>3</sub>-functionalized homopolymer proved to be limited, and redissolving the polymer proved to be difficult, possibly due to the highly charged character of the polymer. However, solubility of the Alq<sub>3</sub>-functionalized polymer could be increased by co-polymerizing **9** with 5-nonylnorbornene **12**, a non-functionalized monomer, which was synthesized as shown in Scheme 3, and presented in the Examples.

Scheme 4



Using comonomers such as compound **12**, Alq<sub>3</sub>-functionalized copolymers could be prepared according to Scheme 4. Znq<sub>2</sub>-functionalized copolymers could be prepared similarly, according to Scheme 4. The other Mq<sub>n</sub>-functionalized copolymers can also be polymerized as indicated in Scheme 4 for the Alq<sub>3</sub> system. Thus, in this aspect, solubility of the Alq<sub>3</sub>-functionalized copolymer exceeded that of the Alq<sub>3</sub>-functionalized homopolymer. However, in one aspect, this invention provides for the formation of an Alq<sub>3</sub>-functionalized homopolymer and further provides for the formation of an Alq<sub>3</sub>-functionalized copolymer, wherein the molar ratio of the functional monomer to spacer monomer is from about 1,000:1 to about 1:1,000. In another aspect, the molar ratio of the functional monomer to spacer monomer is from about 1:1 to about 1:100, and in another aspect, from about 1:3 to about 1:20. In yet another aspect, the molar

ratio of the functional monomer to spacer monomer is from about 1:4 to about 1:10.

In another aspect, the molar ratio of functional monomer to spacer monomer (9:12) was examined to determine ratios wherein 9 can be incorporated in a relatively high percentage, while retaining a useful measure of solubility. This ratio was investigated through the synthesis of a series of co-polymers, as illustrated in Table 1. All co-polymers with a 9:12 ratio of at least about 1:1 could be fully solubilized in a 0.1% (v/v) chloroform/trifluoroacetic acid mixture. All resolubilized co-polymers were characterized using gel-permeation chromatography and showed polydispersities from about 1.5 to about 1.8. Differential scanning calorimetry did not show a glass-transition temperature or a melting temperature for these copolymers, while thermogravimetric analysis showed the onset of polymer decomposition at 250 °C.

**Table 1.** Absorption and Photoluminescence data for 8, Alq<sub>3</sub>, and a series of co-polymers; and co-polymer characterization data for 9:12) polymers.

<i>Sample</i>	<i>UV/Vis conc. (mg/mL)</i>	<i>UV/Vis <math>\lambda_{max}</math> (nm)</i>	<i>Fluorescence conc. (mg/mL)</i>	<i>Fluorescence <math>\lambda_{max}</math> (nm) [Intensity]</i>	<i>Mn</i>	<i>Mw</i>	<i>PDI</i>
Monomer 8	0.02	319	---	---	---	---	---
Alq <sub>3</sub>	0.1	316, 372	0.09	509	---	---	---
1:4 (9:12) Polymer	0.5	313, 370	0.05	512 [2633836]	68000	104000	1.53
1:5 (9:12) Polymer	0.5	313, 371	0.05	509 [2364129]	55000	94000	1.71
1:10 (9:12) Polymer	0.5	313, 373	0.05	506 [1727476]	57000	100000	1.74

In one aspect, this invention provides a composition comprising the polymerization product of an  $Mq_n$ -functionalized monomer, wherein the  $Mq_n$ -functionalized monomer comprises a polymerizable moiety and an  $Mq_n$ -moiety, wherein  $q$ , in each instance, comprises an 8-hydroxyquinoline residue;  $M$  is selected from Mg, Zn, Al, Ga, or In; and  $n$  is selected from 2 or 3 according to the valence of the metal. In another aspect, this polymerization product can be substantially non-crosslinked. Further, and in another aspect, the  $Mq_n$ -moiety can be functionalized with at least one electron-donating group, at least one electron-withdrawing group, or a combination thereof. In another aspect, the polymerizable moiety can comprise norbornene. This invention further provides a light-emitting diode comprising the polymerization product of an  $Mq_n$ -functionalized monomer, wherein the  $Mq_n$ -functionalized monomer comprises a polymerizable moiety and an  $Mq_n$ -moiety, wherein  $q$ , in each instance, comprises an 8-hydroxyquinoline residue;  $M$  is selected from Mg, Zn, Al, Ga, or In; and  $n$  is selected from 2 or 3.

In yet another aspect of this invention, this invention provides a composition comprising the polymerization product of at least one  $Mq_n$ -functionalized monomer and at least one comonomer, wherein the  $Mq_n$ -functionalized monomer comprises a polymerizable moiety and an  $Mq_n$ -moiety; wherein  $q$ , in each instance, comprises an 8-hydroxyquinoline residue;  $M$  is selected from Mg, Zn, Al, Ga, or In; and  $n$  is selected from 2 or 3 according to the valence of the metal. In another aspect, the polymerizable moiety can comprise norbornene, norbornadiene, cyclopentene, cyclooctene, cyclooctadiene, or a substituted analog thereof. In yet another aspect, the polymerizable moiety can comprise norbornene or a substituted analog thereof.

In yet another aspect, this invention provides a composition comprising the polymerization product of at least one  $Mq_n$ -functionalized monomer and at least one comonomer, wherein the  $Mq_n$ -functionalized monomer comprises a polymerizable moiety and an  $Mq_n$ -moiety, and wherein the  $Mq_n$ -moiety can be functionalized with at least one electron-donating group, at least one electron-



withdrawing group, or a combination thereof. In another aspect, the  $Mq_n$ -moiety can be functionalized with at least one group independently selected from: a hydrocarbyl group, an oxygen group, a sulfur group, a nitrogen group, a phosphorus group, an arsenic group, a carbon group, a silicon group, a germanium group, a tin group, a lead group, a boron group, an aluminum group, an inorganic group, an organometallic group, or a substituted analog thereof, any one of which having from 1 to about 30 carbon atoms; a halide; hydrogen; or any combination thereof.

In a further aspect of this invention, the  $Mq_n$ -moiety can be functionalized with at least one group independently selected from -F, -Cl, -Br, -I,  $-R^1$ ,  $-CR^1=O$ ,  $-CH=CHC(O)R^1$ ,  $-C(O)R^1$ ,  $-C(O)OR^1$ , -CN,  $-C(NR^1)R^1$ ,  $-C(NR^1)OR^1$ ,  $-CH_2C_6H_4X$ ,  $-CH_2C_6H_3X_2$ ,  $-CH_2C_6H_4R^1$ ,  $-CH_2C_6H_3R^1_2$ ,  $-CH_2CH_2C_6H_4X$ ,  $-CH_2CH_2C_6H_3X_2$ ,  $-CH_2CH_2C_6H_4R^1$ ,  $-CH_2CH_2C_6H_3R^1_2$ ,  $-CH=CR^1_2$ ,  $-C\equiv CR^1$ ,  $-OR^1$ ,  $-OC(O)R^1$ ,  $-SiR^1_3$ ,  $-OSiR^1_3$ ,  $-NO_2$ ,  $-NR^1_2$ ,  $-N_3$ ,  $-N=CR^1_2$ ,  $-N=NR^1$ ,  $-SR^1$ ,  $-SX$ ,  $-OSO_2R^1$ ,  $-OSO_2OR^1$ ,  $-SCN$ ,  $-SO_2R^1$ ,  $-PR^1_2$ ,  $-PX_2$ ,  $-P(O)R^1_2$ ,  $-P(OR^1)_2$ ,  $-P(O)(OR^1)_2$ ,  $-OSiR^1_3$ ,  $-OPR^1_2$ ,  $-OAlR^1_2$ ,  $-AsR^1_2$ ,  $-As(O)R^1_2$ ,  $-As(OR^1)_2$ ,  $-As(O)(OR^1)_2$ ,  $SnR^1_3$ ,  $OSnR^1_3$ ,  $SnX^1_3$ ,  $OSnX^1_3$ ,  $-BR^1_2$ ,  $-BX_2$ ,  $-BR^1X$ ,  $-SO_2X$ ,  $-OAlX_2$ ,  $-OSiX_3$ ,  $-OPX_2$ ,  $-OSO_2X$ ,  $-AsX_2$ , or  $-As(O)X_2$ ; wherein  $R^1$ , in each instance, is independently selected from H or a substituted or unsubstituted hydrocarbyl group having from 1 to about 30 carbon atoms; and wherein X, in each instance, is independently selected from F, Cl, Br, I, H,  $OR^1$ ,  $-SR^1$ , or  $NR^1_2$ .

In still a further aspect, the  $Mq_n$ -moiety can be functionalized by at least one group independently selected from alkyl, cycloalkyl, alkenyl, alkynyl, aryl, aralkyl, formyl, acyl, imide, amide, imine, alkoxide, aryloxy, alkylthiolate, arylthiolate, alkoxyalkyl, haloalkyl, carboxylate, or a substituted analog thereof, any one of which having up to about 30 carbon atoms.

Still a further aspect of this invention is an  $Mq_n$ -moiety that can be functionalized by at least one group independently selected from methyl, ethyl, propyl, cyclopropyl, n-butyl, tert-butyl, sec-butyl, isobutyl, cyclobutyl, amyl, isoamyl, pentyl, cyclopentyl, hexyl, cyclohexyl, cycloheptyl, heptyl, octyl,

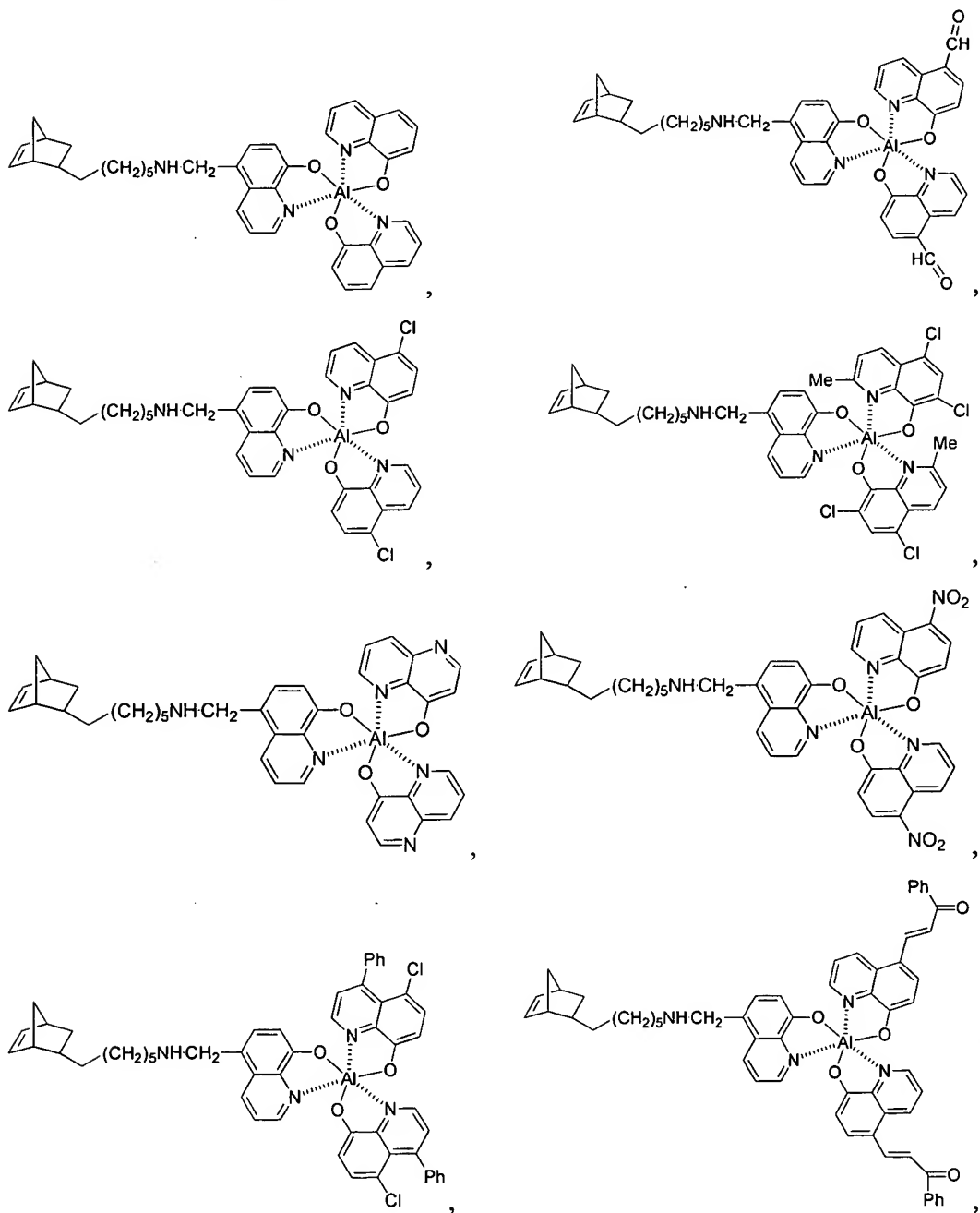
cyclooctyl, nonyl, decyl, dodecyl, 2-ethylhexyl, pentenyl, butenyl, benzyl, phenyl, tolyl, naphthyl, anthracenyl, F, Cl, Br, I, OMe, OEt, O-n-Pr, O-i-Pr, O-n-Bu, O-t-Bu, O-s-Bu, OPh, OC<sub>6</sub>H<sub>4</sub>Me, OC<sub>6</sub>H<sub>3</sub>Me<sub>2</sub>, NMe<sub>2</sub>, NEt<sub>2</sub>, NPh<sub>2</sub>, NHMe, NHEt, NHPh, -CH=O, -CH=CHC(O)Ph, or a substituted analog thereof, any one of  
5 which having up to about 30 carbon atoms.

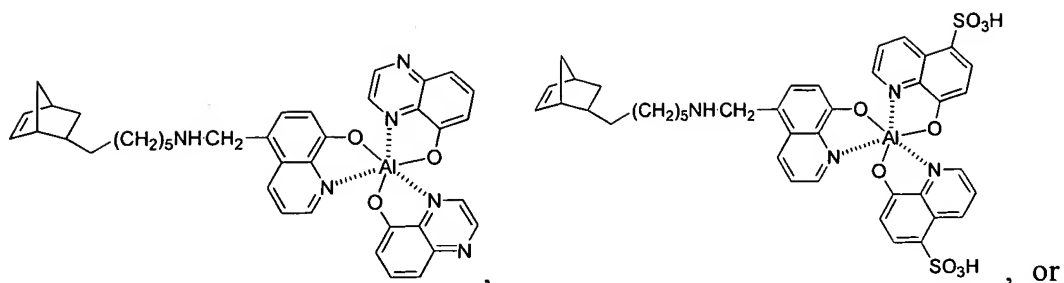
In still another aspect, this invention provides an Mq<sub>n</sub>-functionalized monomer comprising a polymerizable moiety and an Mq<sub>n</sub>-moiety, wherein q, in each instance, comprises an 8-hydroxyquinoline residue, and wherein the Mq<sub>n</sub>-functionalized monomer further comprises a chemical spacer between the  
10 polymerizable moiety and the Mq<sub>n</sub>-moiety, having between 1 and about 30 carbon atoms. In this formula, M is selected from Mg, Zn, Al, Ga, or In; and n is selected from 2 or 3 as dictated by the valence of the metal. Also in this aspect, this invention further provides a composition comprising the polymerization product of at least one Mq<sub>n</sub>-functionalized monomer and at least one comonomer, wherein  
15 the Mq<sub>n</sub>-functionalized monomer comprises a polymerizable moiety and an Mq<sub>n</sub>-moiety, and wherein the Mq<sub>n</sub>-functionalized monomer further comprises a chemical spacer between the polymerizable moiety and the Mq<sub>n</sub>-moiety, having between 1 and about 30 carbon atoms. In one aspect, the chemical spacer can be selected from -(CH<sub>2</sub>)<sub>n</sub>NHCH<sub>2</sub>- or -(CH<sub>2</sub>)<sub>n</sub>NR<sup>1</sup>CH<sub>2</sub>-, wherein n in the formula of  
20 the spacer is from 1 to about 12, and R<sup>1</sup> is selected from a hydrocarbyl or substituted hydrocarbyl having from 1 to about 30 carbon atoms.

In a further aspect, this invention provides the polymerization product of at least one Mq<sub>n</sub>-functionalized monomer and at least one comonomer, wherein the polymerization product comprises a block copolymer. This invention  
25 provides the polymerization product of at least one Mq<sub>n</sub>-functionalized monomer and at least one comonomer, wherein the polymerization product comprises a random copolymer.

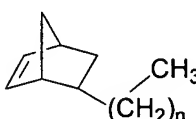
In still a further aspect, this invention provides a composition comprising the polymerization product of at least one Alq<sub>3</sub>-functionalized monomer and at  
30 least one comonomer, wherein the Alq<sub>3</sub>-functionalized monomer comprises a

polymerizable moiety and an Alq<sub>3</sub>-moiety, and wherein q, in each instance, comprises an 8-hydroxyquinoline residue, wherein the Alq<sub>3</sub>-functionalized monomer can be selected from:





any combination thereof. In another aspect, the at least one comonomer can

comprise a compound with the formula , wherein n is an integer from 1 to about 12.

- 5 In a further aspect, this invention provides a composition comprising the polymerization product of at least one  $\text{Alq}_3$ -functionalized monomer and at least one comonomer, wherein the  $\text{Alq}_3$ -functionalized monomer comprises a polymerizable moiety and an  $\text{Alq}_3$ -moiety, and wherein the polymerization product can be characterized by a polydispersity ( $M_w/M_n$ ) from about 1.5 to about
- 10 1.8. In another aspect, this invention provides a light-emitting diode comprising the polymerization product of at least one  $\text{Alq}_3$ -functionalized monomer and at least one comonomer, wherein the  $\text{Alq}_3$ -functionalized monomer comprises a polymerizable moiety and an  $\text{Alq}_3$ -moiety,

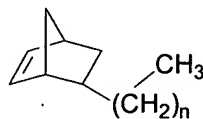
15 In still a further aspect, this invention provides a method of making an  $\text{Mq}_n$ -functionalized polymer, comprising:

polymerizing an  $\text{Mq}_n$ -functionalized monomer in the presence or absence of at least one comonomer;

wherein the  $\text{Mq}_n$ -functionalized monomer comprises a polymerizable moiety and an  $\text{Mq}_n$ -moiety; and

- 20 wherein q, in each instance, comprises an 8-hydroxyquinoline residue; M is selected from Mg, Zn, Al, Ga, or In; and n is selected from 2 or 3 as dictated by the valence of the metal. In another aspect, the  $\text{Mq}_n$ -functionalized monomer can be polymerized in the presence of at least one comonomer. In this aspect, in the method disclosed herein, the  $\text{Mq}_n$ -functionalized monomer can be polymerized in

the presence of at least one comonomer, and wherein the molar ratio of  $Mq_n$ -functionalized monomer to comonomer is from about 1:1 to about 1:20. Also in this aspect, the  $Mq_n$ -functionalized monomer can be polymerized in the presence



of at least one comonomer comprising  $(CH_2)_n$ , wherein  $n$  is an integer from 1 to about 12.

In another aspect, this invention provides a method of making an  $Mq_n$ -functionalized polymer, comprising:

polymerizing an  $Mq_n$ -functionalized monomer in the presence or absence of at least one comonomer;

wherein the  $Mq_n$ -functionalized monomer comprises a polymerizable moiety and an  $Mq_n$ -moiety; wherein the polymerizable moiety of the  $Mq_n$ -functionalized monomer can be selected from norbornene, norbornadiene, cyclopentene, cyclooctene, cyclooctadiene, or a functionalized analog thereof. In this aspect, the method of making an  $Mq_n$ -functionalized polymer can comprise any polymerization method that converts the monomers and optional comonomers into polymers, including, but not limited to, a ring-opening metathesis polymerization (ROMP) method, a radical polymerization method, a controlled radical polymerization method, including, but not limited to, living radical polymerization methods, and the like. *See, for example:* Fischer, H. *Chem. Rev.* **2001**, *101*, 3581-3610; Hawker, C.J.; Bosman, A. W.; Harth, E. *Chem. Rev.* **2001**, *101*, 3661-3688; Kagigaito, M.; Ando, T.; Sawamoto, M. *Chem. Rev.* **2001**, *101*, 3689-3745; each of which is incorporated herein by reference in its entirety.

In still another aspect, the present invention provides a method of making an  $Mq_n$ -functionalized polymer, comprising polymerizing an  $Mq_n$ -functionalized monomer in the presence or absence of at least one comonomer, wherein the polymerization can be conducted in the presence of a catalyst comprising a transition metal carbene compound. In this aspect, the polymerization can be conducted in the presence of any ring-opening metathesis polymerization

(ROMP) catalyst, as long as the monomers, functional groups, or conditions required for polymerization do not terminate the activity of the catalyst. In this aspect, the polymerization can be conducted in the presence of Grubbs' catalysts such as  $\text{Ru}(\text{CHPh})\text{Cl}_2[\text{CHN}_2(\text{mesityl})_2\text{C}_2\text{H}_4](\text{PCy}_3)$  11, as shown in the reaction schemes.

In still another aspect, the present invention provides a method of making an  $\text{Mq}_n$ -functionalized polymer comprising polymerizing an  $\text{Mq}_n$ -functionalized monomer in the presence or absence of at least one comonomer, wherein the  $\text{Mq}_n$ -moiety of the  $\text{Mq}_n$ -functionalized monomer can be functionalized with at least one group independently selected from: a hydrocarbyl group, an oxygen group, a sulfur group, a nitrogen group, a phosphorus group, an arsenic group, a carbon group, a silicon group, a germanium group, a tin group, a lead group, a boron group, an aluminum group, an inorganic group, an organometallic group, or a substituted analog thereof, any one of which having from 1 to about 30 carbon atoms; a halide; hydrogen; or any combination thereof.

In another aspect, this invention provides a method of making an  $\text{Mq}_n$ -functionalized polymer comprising polymerizing an  $\text{Mq}_n$ -functionalized monomer in the presence or absence of at least one comonomer, wherein the  $\text{Mq}_n$ -moiety of the  $\text{Mq}_n$ -functionalized monomer can be functionalized with at least one group independently selected from -F, -Cl, -Br, -I,  $-\text{R}^1$ ,  $-\text{CR}^1=\text{O}$ ,  $-\text{CH}=\text{CHC}(\text{O})\text{R}^1$ ,  $-\text{C}(\text{O})\text{R}^1$ ,  $-\text{C}(\text{O})\text{OR}^1$ , -CN,  $-\text{C}(\text{NR}^1)\text{R}^1$ ,  $-\text{C}(\text{NR}^1)\text{OR}^1$ ,  $-\text{CH}_2\text{C}_6\text{H}_4\text{X}$ ,  $-\text{CH}_2\text{C}_6\text{H}_3\text{X}_2$ ,  $-\text{CH}_2\text{C}_6\text{H}_4\text{R}^1$ ,  $-\text{CH}_2\text{C}_6\text{H}_3\text{R}^1_2$ ,  $-\text{CH}_2\text{CH}_2\text{C}_6\text{H}_4\text{X}$ ,  $-\text{CH}_2\text{CH}_2\text{C}_6\text{H}_3\text{X}_2$ ,  $\text{CH}_2\text{CH}_2\text{C}_6\text{H}_4\text{R}^1$ ,  $-\text{CH}_2\text{CH}_2\text{C}_6\text{H}_3\text{R}^1_2$ ,  $-\text{CH}=\text{CR}^1_2$ ,  $-\text{C}\equiv\text{CR}^1$ ,  $-\text{OR}^1$ ,  $-\text{OC}(\text{O})\text{R}^1$ ,  $-\text{SiR}^1_3$ ,  $-\text{OSiR}^1_3$ ,  $-\text{NO}_2$ ,  $-\text{NR}^1_2$ ,  $-\text{N}_3$ ,  $-\text{N}=\text{CR}^1_2$ ,  $-\text{N}=\text{NR}^1$ ,  $-\text{SR}^1$ ,  $-\text{SX}$ ,  $-\text{OSO}_2\text{R}^1$ ,  $-\text{OSO}_2\text{OR}^1$ ,  $-\text{SCN}$ ,  $-\text{SO}_2\text{R}^1$ ,  $-\text{PR}^1_2$ ,  $-\text{PX}_2$ ,  $-\text{P}(\text{O})\text{R}^1_2$ ,  $-\text{P}(\text{OR}^1)_2$ ,  $-\text{P}(\text{O})(\text{OR}^1)_2$ ,  $-\text{OSiR}^1_3$ ,  $-\text{OPR}^1_2$ ,  $-\text{OAlR}^1_2$ ,  $-\text{AsR}^1_2$ ,  $-\text{As}(\text{O})\text{R}^1_2$ ,  $-\text{As}(\text{OR}^1)_2$ ,  $-\text{As}(\text{O})(\text{OR}^1)_2$ ,  $\text{SnR}^1_3$ ,  $\text{OSnR}^1_3$ ,  $\text{SnX}^1_3$ ,  $\text{OSnX}^1_3$ ,  $-\text{BR}^1_2$ ,  $-\text{BX}_2$ ,  $-\text{BR}^1\text{X}$ ,  $-\text{SO}_2\text{X}$ ,  $-\text{OAlX}_2$ ,  $-\text{OSiX}_3$ ,  $-\text{OPX}_2$ ,  $-\text{OSO}_2\text{X}$ ,  $-\text{AsX}_2$ , or  $-\text{As}(\text{O})\text{X}_2$ ; wherein  $\text{R}^1$ , in each instance, is independently selected from H or a substituted or unsubstituted hydrocarbyl group having from 1 to about 30 carbon atoms; and

wherein X, in each instance, is independently selected from F, Cl, Br, I, H, OR<sup>1</sup>, -SR<sup>1</sup>, or NR<sup>1</sup><sub>2</sub>.

In yet another aspect, this invention provides a method of making an Mq<sub>n</sub>-functionalized polymer comprising polymerizing an Mq<sub>n</sub>-functionalized monomer  
5 in the presence or absence of at least one comonomer, wherein the Mq<sub>n</sub>-moiety of the Mq<sub>n</sub>-functionalized monomer can be functionalized with at least one group independently selected from alkyl, cycloalkyl, alkenyl, alkynyl, aryl, aralkyl, formyl, acyl, imide, amide, imine, alkoxide, aryloxy, alkylthiolate, arylthiolate, alkoxyalkyl, haloalkyl, carboxylate, or a substituted analog thereof, any one of  
10 which having up to about 30 carbon atoms.

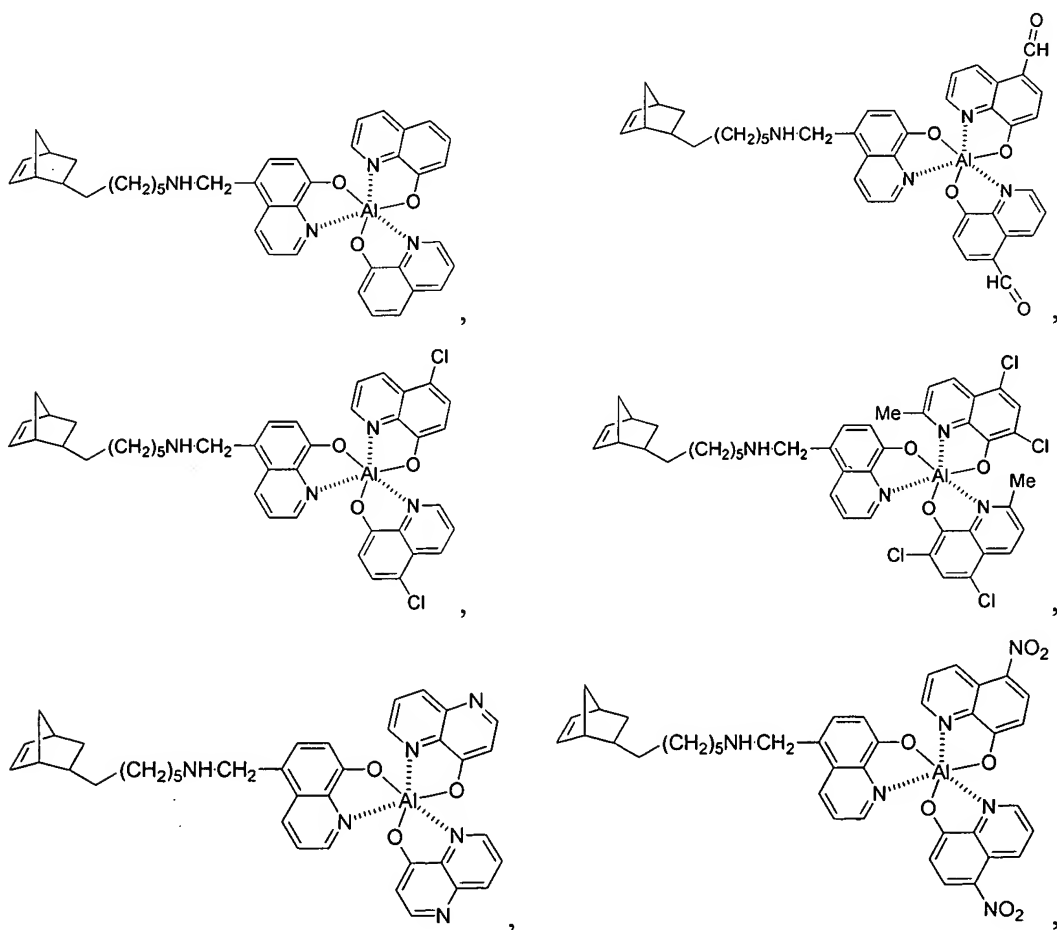
In still another aspect, this invention provides a method of making an Mq<sub>n</sub>-functionalized polymer comprising polymerizing an Mq<sub>n</sub>-functionalized monomer in the presence or absence of at least one comonomer, wherein the Mq<sub>n</sub>-moiety of the Mq<sub>n</sub>-functionalized monomer can be functionalized with at least  
15 one group independently selected from methyl, ethyl, propyl, cyclopropyl, n-butyl, tert-butyl, sec-butyl, isobutyl, cyclobutyl, amyl, isoamyl, pentyl, cyclopentyl, hexyl, cyclohexyl, cycloheptyl, heptyl, octyl, cyclooctyl, nonyl, decyl, dodecyl, 2-ethylhexyl, pentenyl, butenyl, benzyl, phenyl, tolyl, naphthyl, anthracenyl, F, Cl, Br, I, OMe, OEt, O-n-Pr, O-i-Pr, O-n-Bu, O-t-Bu, O-s-Bu,  
20 OPh, OC<sub>6</sub>H<sub>4</sub>Me, OC<sub>6</sub>H<sub>3</sub>Me<sub>2</sub>, NMe<sub>2</sub>, NEt<sub>2</sub>, NPh<sub>2</sub>, NHMe, NHEt, NHPh, -CH=O, -CH=CHC(O)Ph, or a substituted analog thereof, any one of which having up to about 30 carbon atoms.

In another aspect, this invention provides a method of making an Alq<sub>3</sub>-functionalized polymer comprising polymerizing an Alq<sub>3</sub>-functionalized  
25 monomer in the presence or absence of at least one comonomer, wherein the Alq<sub>3</sub>-functionalized monomer further comprises a chemical spacer between the polymerizable moiety and the Alq<sub>3</sub>-moiety, having between 1 and about 30 carbon atoms. In another aspect, for example, the chemical spacer can be selected from -(CH<sub>2</sub>)<sub>n</sub>NHCH<sub>2</sub>- or -(CH<sub>2</sub>)<sub>n</sub>NR<sup>1</sup>CH<sub>2</sub>-, wherein n in the chemical spacer

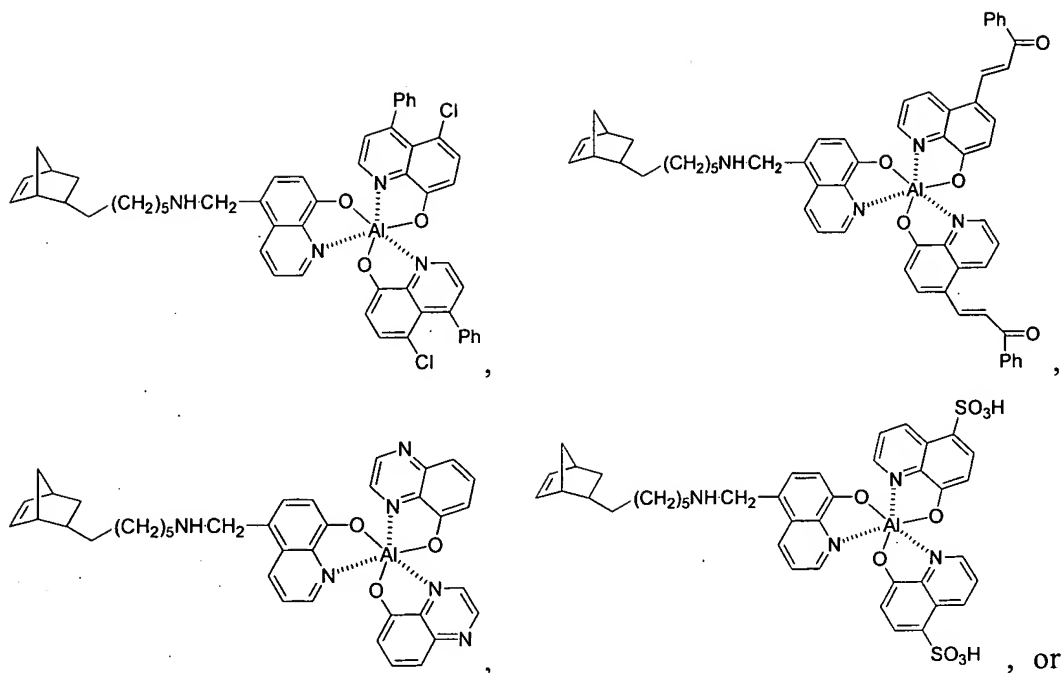
formula is from 1 to about 12, and R<sup>1</sup> is selected from a hydrocarbyl or substituted hydrocarbyl having from 1 to about 30 carbon atoms.

In still another aspect, this invention provides a method of making an Alq<sub>3</sub>-functionalized polymer comprising polymerizing an Alq<sub>3</sub>-functionalized monomer in the presence or absence of at least one comonomer, wherein the polymerization product comprises a block copolymer.

In another aspect, this invention provides a method of making an Alq<sub>3</sub>-functionalized polymer comprising polymerizing an Alq<sub>3</sub>-functionalized monomer in the presence or absence of at least one comonomer, wherein the Alq<sub>3</sub>-functionalized monomer is selected from:







any combination thereof.

In yet another aspect, the present invention provides a method of functionalizing a polymer with an Alq<sub>3</sub> moiety, comprising:

providing an Alq<sub>3</sub>-functionalized monomer; and

polymerizing an Alq<sub>3</sub>-functionalized monomer in the presence or absence of at least one comonomer;

wherein the Alq<sub>3</sub>-functionalized monomer comprises a polymerizable moiety and an Alq<sub>3</sub>-moiety; and

wherein q, in each instance, comprises an 8-hydroxyquinoline residue.

#### Optical Properties of Selected Mq<sub>n</sub>-Functionalized Polymers

The photoluminescence of the Alq<sub>3</sub>-functionalized copolymers and monomer 9 were investigated and compared to the photoluminescence of Alq<sub>3</sub> itself. As a measure of the baseline performance of the copolymers and monomer 9, commercial Alq<sub>3</sub> was treated with the same chloroform/trifluoroacetic acid mixture as the copolymers. No changes were detected in the optical properties of

Alq<sub>3</sub> after this treatment, as compared to the optical properties of Alq<sub>3</sub> before this treatment.

The UV/Visible absorption spectrum of monomer **9** shows a  $\lambda_{\max}$  at 319 nm, corresponding to the low-energy singlet transition of the hydroxyquinoline group. (See: Ravi Kishore, V. V. N.; Aziz, A.; Narasimhan, K. L.; Periasamy, N.; Meenakshi, P. S.; Wategaonkar, S. *Synth. Met.* **2002**, *126*, 199-205, which is incorporated by reference herein, in its entirety.) The absorption spectrum of Alq<sub>3</sub> showed peaks at 372 nm and at 316 nm, consistent with the reported spectrum. (See: Halls, M. D.; Schlegel, H. B. *Chem. Mater.* **2001**, *13*, 2632-2640, which is incorporated by reference herein, in its entirety.) Figure 1 illustrates the UV/Visible absorption spectra of Alq<sub>3</sub>, the Alq<sub>3</sub>-containing monomer **9**, and the series of **9**:**12** copolymers in CHCl<sub>3</sub> solution, as described in Table 1. The absorption spectra of all the copolymers examined showed identical peaks as that of Alq<sub>3</sub>, indicating the same transitions taking place in the copolymer system as the ones known for Alq<sub>3</sub>. Absorption and photoluminescence data for **9**, Alq<sub>3</sub>, and a series of co-polymers recorded on relatively dilute solutions are presented in Table 2, as compared to the data recorded in Table 1.

**Table 2.** Absorption and photoluminescence data for **9**, Alq<sub>3</sub>, and a series of **9**:**12** co-polymers recorded on relatively dilute solutions.

Sample	UV/Vis conc. (mg/mL)	UV/Vis $\lambda_{\max}$ (nm)	Fluorescence conc. (mg/mL)	Fluorescence $\lambda_{\max}$ (nm)
Monomer <b>9</b>	0.045	319	NA	NA
Alq <sub>3</sub>	0.12	316, 372	0.009	506
1:4 Polymer	0.20	313, 375	0.020	506
1:5 Polymer	0.058	314, 378	0.023	505
1:10 Polymer	0.072	314, 378	0.028	512

The emission spectra of Alq<sub>3</sub> and the copolymers were collected from 400-700 nm, with an excitation wavelength of 380 nm. Figure 2 illustrates the emission spectra of Alq<sub>3</sub> and the series of 9:12 copolymers in CHCl<sub>3</sub> solution, excited at 380 nm, as described in Table 1. As shown in Figure 2, all copolymers fluoresce at the same wavelength as Alq<sub>3</sub> in solution, demonstrating that the emission properties of Alq<sub>3</sub> are retained in the polymer matrix.

The ratio of Alq<sub>3</sub>-monomer to the non-functionalized monomer in the copolymers affected the intensity of the emission. Thus the intensity showed a linear relationship with the percentage of Alq<sub>3</sub> present in the copolymer, as indicated by the data provided in Table 1. While not intending to be bound by theory, these studies suggest that the optical properties of Alq<sub>3</sub> are preserved in the polymer and not affected by the polymer coil while in solution. Upon spin-casted the copolymer solutions to provide thin films of the Alq<sub>3</sub>-functionalized polymer, the resulting films exhibited fluorescence emission similar to that of Alq<sub>3</sub> in the solid state. Table 2 provides absorption and photoluminescence data for 9, Alq<sub>3</sub>, and a series of co-polymers recorded on relatively dilute solutions, as compared to the data recorded in Table 1.

While not intending to be bound by theory, when comparing Alq<sub>3</sub>-functionalized polymers to the other Mq<sub>n</sub>-functionalized polymers, fluorescence is generally expected to be reduced with increasing atomic number of the metal ion, which is referred to as the heavy atom effect. In addition, as the covalent bond character between metal and quinoline ligand increases, the Mq<sub>n</sub> complexes are expected to become more red shifted. For example, and again while not intending to be bound by theory, the analogous Al, Ga, and In complexes would be expected to emit at progressively longer wavelengths (red shifted). *See, for example:* Chen, C. H.; Shi, J. *Coord. Chem. Rev.* **1998**, *171*, 161-174, which is incorporated herein by reference in its entirety.

### Preparation of Selected $Mq_n$ -Functionalized Polymers With an Electronically-Tuned Ligand Sphere

Another aspect of this invention is an  $Mq_n$ -functionalized polymer with an electronically-tuned ligand sphere about the metal center. In this aspect, this invention provides a composition comprising the polymerization product of an  $Mq_n$ -functionalized monomer, wherein the  $Mq_n$ -functionalized monomer can comprise a polymerizable moiety and an  $Mq_n$ -moiety, wherein q, in each instance, comprises an 8-hydroxyquinoline residue, and M is selected from Mg, Zn, Al, Ga, or In; and n is selected from 2 or 3 according to the valence of the metal. Further to this aspect, this invention provides a composition comprising the polymerization product of an  $Alq_3$ -functionalized monomer, which can comprise a polymerizable moiety and an  $Alq_3$ -moiety, and wherein q, in each instance, comprises an 8-hydroxyquinoline residue, which, in accordance with this invention, can include a residue of an 8-hydroxyquinoline-like compound, or a functionalized analog of an an 8-hydroxyquinoline or an 8-hydroxyquinoline-like compound. Further in this aspect, the  $Alq_3$ -moiety of the  $Alq_3$ -functionalized monomer can be functionalized with at least one electron-donating group, at least one electron-withdrawing group, or a combination thereof. For example, the ligand sphere around the aluminum center on the polymer can be functionalized with electron-donating or withdrawing groups thereby allowing the emission of the polymer to be tuned from blue to yellow (from about 430 nm to about 549 nm).

In one aspect, this invention provides the ability to tune the emission of the  $Alq_3$ -functionalized monomer, and hence the  $Alq_3$ -functionalized polymer, according to the functionalization of the ligand sphere around the aluminum center on the polymer with electron-donating, withdrawing groups, or a combination thereof.

In one aspect, this invention provides for the modification of the 8-hydroxyquinoline ligand with electron-donating or withdrawing groups, thereby changing the HOMO-LUMO gap of the substituted 8-hydroxyquinoline ligands.

(See, for example: Hopkins, T. A.; Meerholz, K.; Shaheen, S.; Anderson, M. L.; Schmidt, A.; Kippelen, B.; Padias, A. B.; H.K. Hall, J.; Peyghambarian, N.; Armstrong, N. R. *Chem. Mater.* **1996**, *8*, 344-351; Jang, H.; Do, L.-M.; Kim, Y.; Zyung, T.; Do, Y. *Synth. Met.* **2001**, *121*, 1667-1668; each of which is  
5 incorporated by reference herein in its entirety.)

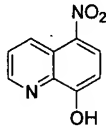
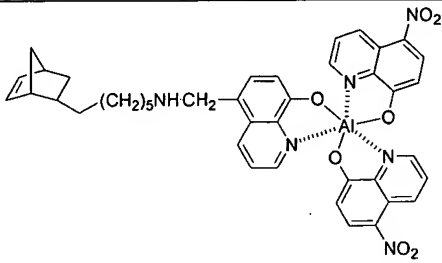
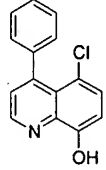
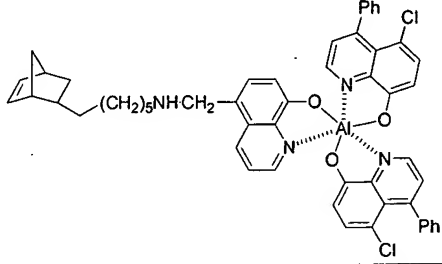
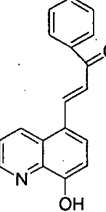
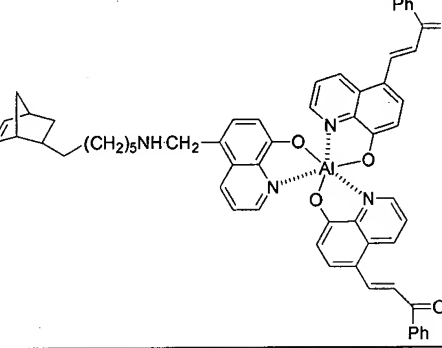
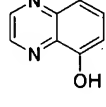
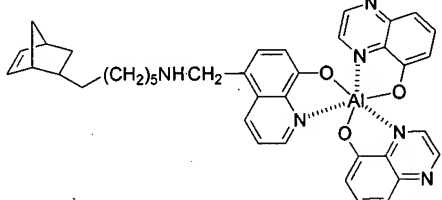
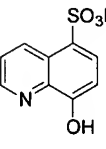
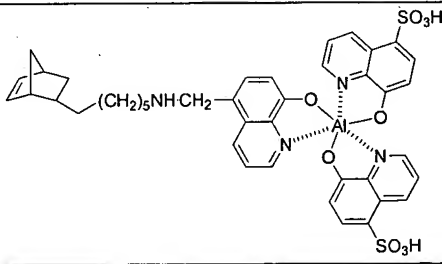
In still another aspect, this invention provides for the introduction of heteroatoms into the 8-hydroxyquinoline ring system, which can have a profound effect on the electronic structure and the resulting the emission of the corresponding  $Mq_n$ -functionalized monomer and  $Mq_n$ -functionalized polymer. In  
10 this aspect, for example, substitution of a nitrogen atom in an 8-hydroxyquinoline ring system, including, but not limited to the 4- or 5-position, can result in either a large blue-shift or a large red-shift respectively. Also in this aspect, terms such as  $Mq_n$ ,  $Mq_n$ -functionalized compound,  $Mq_n$ -functionalized polymer, 8-hydroxyquinoline ligand, and the like, are used to refer to  $Mq_n$ -like compounds  
15 and 8-hydroxyquinoline ligands that are modified with electron-donating or withdrawing groups, and are similarly used to refer to  $Alq_3$ -like compounds and 8-hydroxyquinoline ligands that are modified by introduction of heteroatoms into the 8-hydroxyquinoline ring system.

The synthesis of the modified  $Alq_3$ -functionalized monomers is shown in  
20 Scheme 5, in which the 8-hydroxyquinoline ring system is modified with electron-donating or withdrawing groups, or by the introduction of heteroatoms into the 8-hydroxyquinoline ring system. The structures of the resulting monomers are illustrated in Table 3. The functionalized 8-hydroxyquinoline ligands employed in this Scheme, represented by "X", are shown in Figure 3,  
25 along with the abbreviations used to designate these ligands. Thus, as illustrated in Scheme 5, the typical modified  $Alq_3$ -containing monomer has one 8-hydroxyquinoline ligand coordinating the aluminum that derived from the polymerizable molecule comprising a norbornene moiety, while the other two 8-hydroxyquinoline ligands constitute the 8-hydroxyquinoline ring systems that are  
30 modified with electron-donating or withdrawing groups, or by the introduction of

heteroatoms. A large number of these functionalized 8-hydroxyquinoline molecules are commercially available from, for example, LaboTest (Niederschöna, Germany) and can be used in this invention.

5 **Table 3.** Functionalized Alq<sub>3</sub>-Containing Monomers

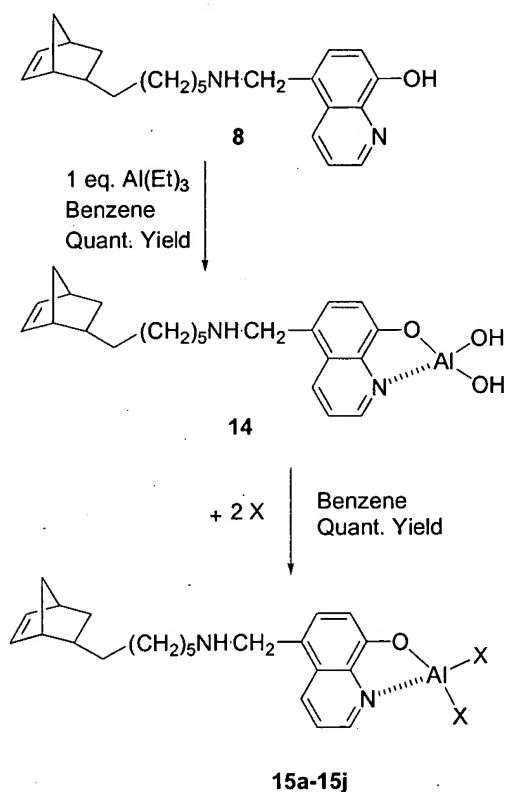
Compound Number	Ligand X	Monomer Structure	Ligand X Abbreviation
15a			Alq <sub>3</sub>
15b			CHO
15c			Cl
15d			MeCl <sub>2</sub>
15e			Naph

15f			NO <sub>2</sub>
15g			Ph
15h			PVK
15i			Quinox
15j			SO <sub>3</sub> H

As illustrated in Scheme 5 and in the Examples, metallation of monomer **8** was carried out by the addition of **8** to a solution of triethylaluminum, resulting in the formation of the metallated monomer **14**. The addition of two equivalents of the modified 8-hydroxyquinoline ligands **X** to monomer **14** resulted in the

formation of monomers **15a-15j** (referred to generically as **15**) in quantitative yields. Examples of the functionalized 8-hydroxyquinoline ligands include, but are not limited to, those ligands shown in Figure 3 and Table 3.

Scheme 5



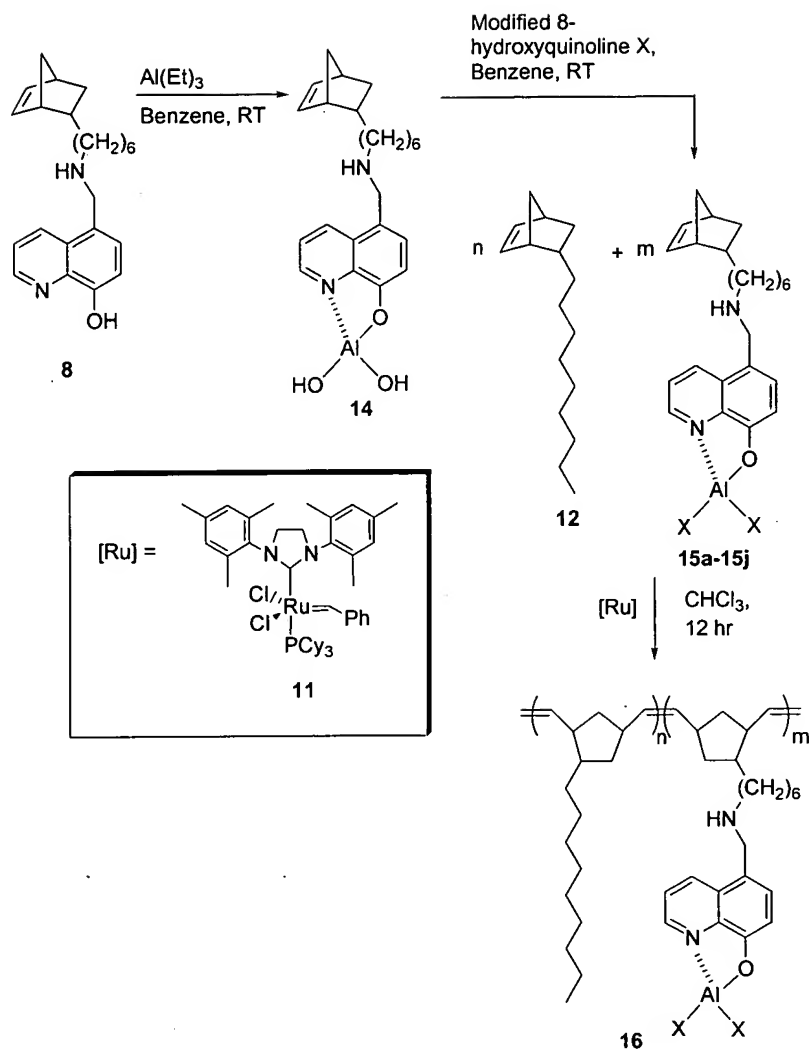
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Scheme 6 illustrates that polymerizations were carried out by combining **12** and **15** in chloroform and adding catalyst **11**. Thus, co-polymerization with nonylnorbornene was employed to render all polymers highly soluble in common organic solvents. In one aspect, a molar ratio of  $\text{AlqX}_2$ -monomer to nonylnorbornene of about 1:20 was used in all fluorescence studies unless otherwise noted, which provided good results.

10

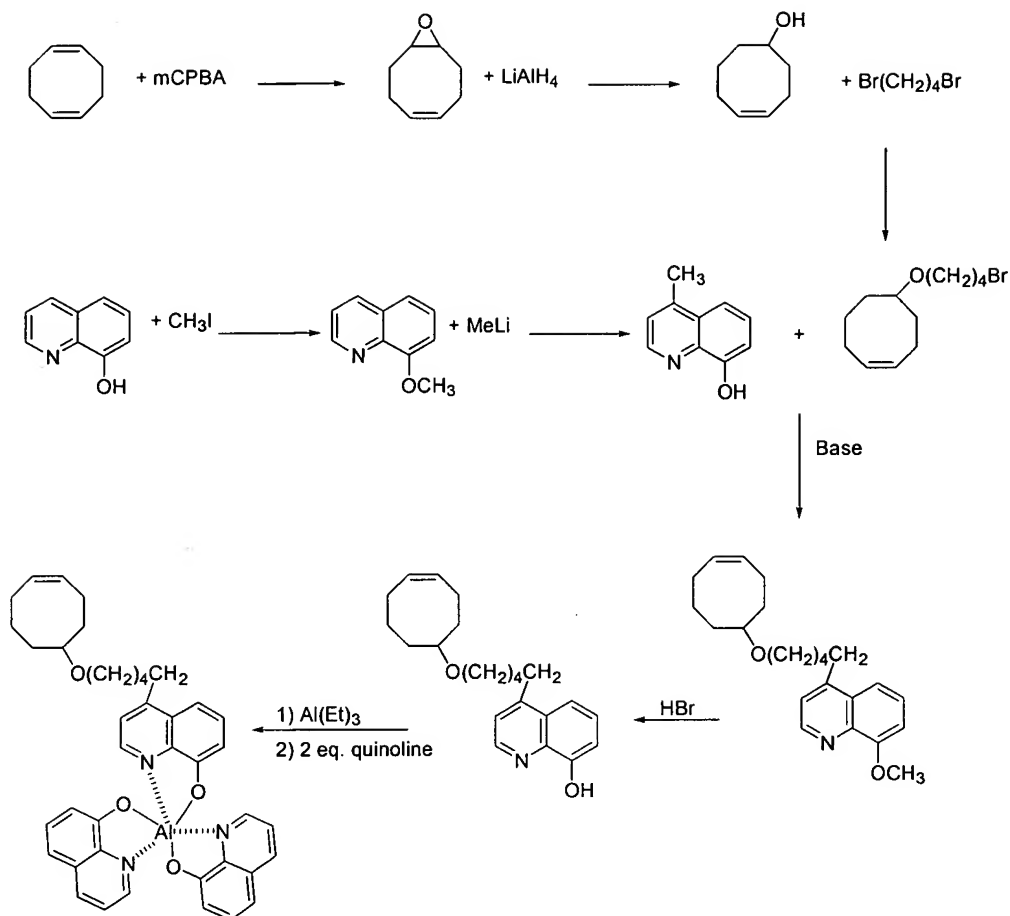


Scheme 6



In still another aspect, this invention provides for the use of a variety of polymerizable moieties other than norbornene to be used in the preparation of the  $\text{Mq}_n$ -functionalized monomers and the  $\text{Mq}_n$ -functionalized polymers. In one aspect, for example, the preparation of an  $\text{Alq}_3$ -functionalized monomer, comprising a cyclooctene polymerizable moiety, is presented in Scheme 7. The preparation provided in Scheme 7 is applicable to the range of  $\text{Mq}_n$ -functionalized monomers and the  $\text{Mq}_n$ -functionalized polymers.

Scheme 7

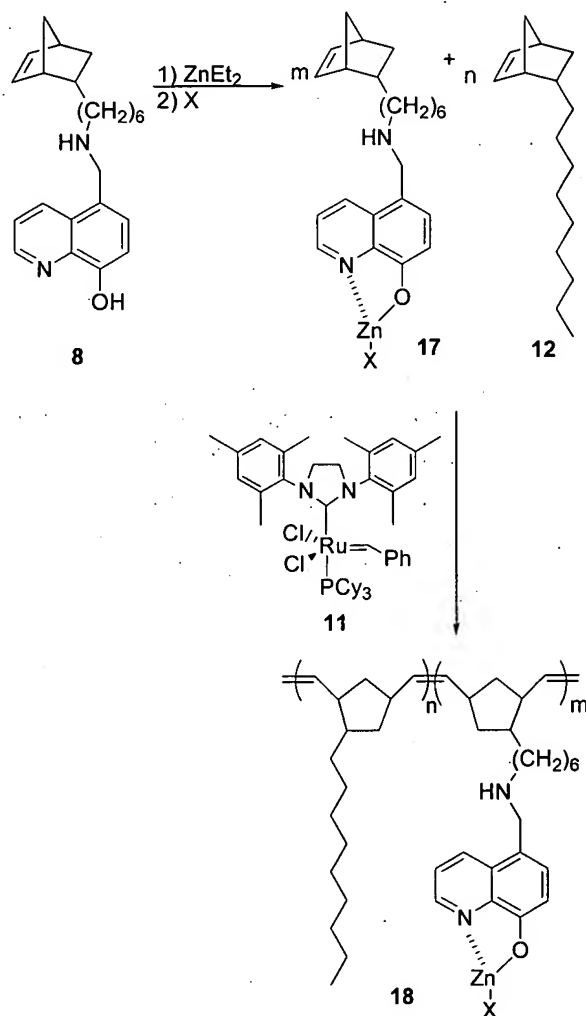


In still another aspect, this invention provides for the preparation of zinc-  
 containing monomers and polymers, as illustrated in Scheme 8. Thus, Scheme 8  
 illustrates that polymerizations were carried out by combining **12** and **17** in  
 solution and adding catalyst **11**. Thus, co-polymerization with nonylnorbornene  
 was employed to render all polymers highly soluble in common organic solvents.  
 In one aspect, a molar ratio of Znq<sub>2</sub>-monomer or ZnqX-monomer to  
 nonylnorbornene of about 1:20 was used in all fluorescence studies unless  
 otherwise noted, which provided good results. As in the aluminum compounds,  
 the design, synthesis, and characterization of the Znq<sub>2</sub>-copolymers, demonstrated  
 excellent photoluminescence properties, with emission wavelengths ranging from

the blue to the yellow, while retaining the solution processability. Accordingly, these copolymers could be used in electroluminescent devices.

To examine and improve solubilities, monomer **8** was co-polymerized with a spacer monomer, nonylnorbornene **12**, in ratios of 1:1, 1:5, 1:10, and 1:20 (8/12), resulting in copolymers that were readily soluble. The 1:20 ratios were used to characterize the optical properties of the copolymers, unless otherwise noted.

Scheme 8



### Chemical, Physical, and Optical Properties of Alq<sub>3</sub>-Functionalized Polymers With an Electronically-Tuned Ligand Sphere

The Alq<sub>3</sub>-functionalized polymers with electronically-tuned ligand spheres were characterized by NMR, gel-permeation chromatography (GPC), differential scanning calorimetry (DSC), and thermogravimetric analysis (TGA), with the results summarized in Table 4. The polymerizations were followed by NMR and were considered complete when no olefin signals were detected. In one aspect, the molecular weights of the polymers, determined by GPC, ranged from about 7000 to about 55000, with polydispersities (PDI) from about 1.26 to about 2.74. All polymers showed a decomposition temperature around 250 °C, with no glass transition or any other endotherms being detected under the conditions used.

**Table 4.** The monomer molar ratios, modified ligands, and molecular weight and polydispersity properties of Alq<sub>3</sub>-functionalized polymers of this invention.

<i>Polymer<sup>a</sup></i>	<i>m/n ratio</i>	<i>X</i>	<i>M<sub>n</sub></i>	<i>M<sub>w</sub></i>	<i>PDI</i>
Alq <sub>3</sub> 110	1:10	Alq <sub>3</sub>	11000	16300	1.47
Alq <sub>3</sub> 120	1:20	Alq <sub>3</sub>	7600	11600	1.53
Alq <sub>3</sub> 150	1:50	Alq <sub>3</sub>	24000	58400	2.43
Alq <sub>3</sub> 500mer <sup>b</sup>	1:20	Alq <sub>3</sub>	10400	18600	1.77
Alq <sub>3</sub> 1000mer <sup>b</sup>	1:20	Alq <sub>3</sub>	19400	35400	1.82
Bu	1:20	Bu	6600	16100	2.46
CHO110	1:10	CHO	14200	29200	2.06
CHO120	1:20	CHO	24200	52600	2.16
CHO150	1:50	CHO	19000	42600	2.24
Cl	1:20	Cl	17500	43000	2.45
MeCl <sub>2</sub>	1:20	MeCl <sub>2</sub>	15000	28700	1.92
Naph120	1:20	Naph	21100	35100	1.67
NO <sub>2</sub>	1:20	NO <sub>2</sub>	11000	17000	1.56
Ph	1:20	Ph	17300	38300	2.21

PVK110	1:10	PVK	14500	27500	1.89
PVK120	1:20	PVK	10200	20800	2.04
PVK150	1:50	PVK	20000	55000	2.74
Quinox	1:20	Quinox	15600	31200	1.99
SO <sub>3</sub> H	1:20	SO <sub>3</sub> H	4700	7700	1.63

<sup>a</sup> Polymers are named after the functionalized ligand **X** and the molar ratio of **15:12**. If a number is not present, then the polymer was composed of a 1:20 **15:12** ratio.

<sup>b</sup> 500mer and 1000mer refer to the number of repeat units in the polymer.

5

### Solution Fluorescence Studies on Alq<sub>3</sub> Complexes

The normalized solution emission spectra of selected modified polymers in chloroform are presented in Figure 4. Solution emission results are also summarized in Table 5. The unmodified Alq<sub>3</sub>-polymer (**Alq<sub>3</sub>**) was observed to emit at the same wavelength as pure Alq<sub>3</sub> (523 nm). Similar to modified-Alq<sub>3</sub>, the polymers containing functionalized Alq<sub>3</sub> side-chains show either a blue- or red-shifted emission, depending on the functionalization. While most of the modified 8-hydroxyquinoline ligands induce shifts in the emission spectra, the most noticeable shifts result from polymers functionalized with either the 4-hydroxy-1,5-naphthyridine (**Naph**) or the quinoxalinol (**Quinox**) ligands. The naphthyridine ligand induces a strong blue-shifted of about 90 nm, while the quinoxalinol ligand induces a red-shifted of about 50 nm. Other dramatic shifts occurred after functionalization with the aldehyde-functionalized ligand (**CHO**) (-32 nm) and the phenyl-vinyl-ketone-functionalized ligand (**PVK**) (+21 nm).

Less dramatic blue- or red-shifts were observed for the polymers based on dichloromethyl- (**MeCl<sub>2</sub>**), chloride- (**Cl**), and sulfonic acid- (**SO<sub>3</sub>H**) functionalized hydroxyquinolines. The phenyl-functionalized (**Ph**) polymer was observed not to shift the emission wavelength, perhaps because the donating ability of the phenyl group was offset by the withdrawing ability of the chloride group. The nitro-polymer (**NO<sub>2</sub>**) did show a 20 nm blue-shift, but the intensity of

this emission was very low in comparison to all other polymers. While not intending to be bound by theory, these shifts can be rationalized by considering the electron-donating and electron-withdrawing ability of the substituents on the modified ligands.

5

**Table 5.** Excitation and emission wavelength for the polymers in solution and the solid-state.

<i>Polymer</i> <sup>a</sup>	<i>Excitation <math>\lambda</math></i> (nm)	<i>Solution</i> <i>Emission <math>\lambda_{max}</math></i> (nm)	<i>Solid-State</i> <i>Emission <math>\lambda_{max}</math></i> (nm)
Alq <sub>3</sub>	380	523	511
Bu	380	522	515
CHO	380	488	510
Cl	380	537	520
MeCl <sub>2</sub>	380	510	505
Naph	330	430, 490	437, 498
NO <sub>2</sub>	380	510	n/a
Ph	380	523	n/a
PVK	380	543	537
Quinox	400	570	n/a
SO <sub>3</sub> H	380	508	495
Alq500mer <sup>b</sup>	380	523	510
Alq1000mer <sup>b</sup>	380	522	512

<sup>a</sup> Polymers are named after the functionalized ligand **X**; all polymers comprise a 1:20 ratio of **15:12**.

10 <sup>b</sup> 500mer and 1000mer refer to the number of repeat units in the polymer.

The emission spectrum of the **Naph**-polymer shows two maxima, one at 430 nm and the other one at 490 nm. The two maxima can be attributed to the two different ligands around the aluminum center, namely, two naphthyridine

ligands and one hydroxyquinoline ligand. Again, while not intending to be bound by theory, it is likely that the peak at 430 nm arises from an oriented naphthyridine ligand, while the emission peak at 490 nm arises from the hydroxyquinoline ligand. The electronics of the hydroxyquinoline ligand are affected by the naphthyridine ligand, resulting in a blue-shift from the usual 520 nm. This idea was tested by preparing the small molecule counterpart containing two naphthyridine ligands and one hydroxyquinoline ligand around an aluminum center. The emission spectrum of this compound was identical to that of the polymer. This two ligand effect can also be seen in the **CHO**-polymer, with a small shoulder occurring at 450 nm.

These data from the solution emission studies suggest that the polymer backbone does not interfere with the optical properties of the Alq<sub>3</sub> side-chain, and that the emission can be tuned through simple ligand modifications.

Thus, in one aspect of this invention, using electron-donating or electron-withdrawing ligands that can shift the photoluminescence, the emission of the functionalized polymers can be tuned in solution as well as in the solid-state from ranging from about 490 nm up to about 550 nm. The intensity of the solid-state emission can also be altered by adjusting the concentration of the polymer solution before spin-casting, while the emission wavelength can be shifted up to about 30 nm by changing the chromophore density.

#### Thin-Film Characterization of Alq<sub>3</sub>-Containing Polymers

Thin films of the functionalized Alq<sub>3</sub>-containing polymers were fabricated by spin coating techniques and were characterized using optical microscopy, ellipsometry, and fluorescence spectroscopy. The thicknesses of the films ranged from about 200 nm to about 600 nm depending on the concentration of the polymer solution. The uniformity of the films was observed using an inverted microscope while irradiating the films with UV light. These observations indicated that all of the films showed very smooth surfaces with good uniformity and very few defects.

Experiments were conducted to determine if the functionalized Alq<sub>3</sub>-containing polymers could support a current. Thin films of 1:5, 1:10, and 1:20 Alq<sub>3</sub>-copolymers were characterized. All three films were conductive, with the conductivity ranging between 4-12 S/cm and the highest conductivity for the 1:5 Alq<sub>3</sub> copolymer, as shown in Table 6. This observation suggests that the polymer system of this invention can be used as the electron-transport and emission layer in OLEDs.

**Table 6.** Resistivity measurements and calculated conductivity of the Alq<sub>3</sub>-polymers.

<i>Polymer<sup>a</sup></i>	<i>Resistivity (<math>\Omega</math>)</i>	<i>Thickness (cm)</i>	<i>Conductivity (S/cm)</i>
Alq <sub>3</sub> 15	46	0.00042	12
Alq <sub>3</sub> 110	61	0.00039	9
Alq <sub>3</sub> 120	92	0.00061	4

<sup>a</sup> Polymers are named after the functionalized ligand **X** and the ratio of **15:12**. For example Alq<sub>3</sub> 110 is a 1:10 molar ratio of compound **15:12**, wherein the ligand is Alq<sub>3</sub>.

#### Solid-State Fluorescence Studies of Alq<sub>3</sub>-Functionalized Polymers

The optical properties of all Alq<sub>3</sub>-functionalized polymers were also investigated in the solid-state. Unless otherwise noted, all polymers were excited at 380 nm (except for the **Naph**- and **Quinox**-polymers, which were excited at 330 nm and 400 nm, respectively) and their emission data are shown in Table 7. Figure 5 shows the normalized fluorescence spectra of selected polymers as thin films on quartz. In the case of each functionalized polymer observed, spectra were observed to show shifts in the emission compared to the unmodified Alq<sub>3</sub>-polymer. However, in all cases, the shifts were not as pronounced as the shifts observed for the same polymer in solution. Furthermore, under the conditions



employed, the **Nitro-**, **Quinox-**, and **Phenyl-**polymers showed no emission at all. Nevertheless, the observed shifts demonstrate that tuning the emission color is possible and that the polymer backbone does not inhibit fluorescence even in the solid-state.

5

**Table 7.** Solution and solid-state emission wavelength for the polymers of varying chromophore ratios.

<i>Polymer<sup>a</sup></i>	<i>Excitation <math>\lambda</math> (nm)</i>	<i>Solution Emission <math>\lambda_{max}</math> (nm)</i>	<i>Solid-State Emission <math>\lambda_{max}</math> (nm)</i>
Alq <sub>3</sub> 110	380	522	522
Alq <sub>3</sub> 120	380	523	511
Alq <sub>3</sub> 150	380	522	502
CHO110	380	486	522
CHO120	380	488	510
CHO150	380	487	494
PVK110	380	543	549
PVK120	380	543	537
PVK150	380	544	530

<sup>a</sup> Polymers are named after the functionalized ligand **X** and the molar ratio of **15:12**.

10

In order to investigate the influence of chromophore density on the emission, the ratio of the AlqX<sub>2</sub>-monomer and nonylnorbornene was varied. The results of this study are shown in Figures 6-8 and are summarized in Table 7. Figure 6 illustrates the solid-state fluorescence spectra of the Alq<sub>3</sub>-polymer with functionalized Alq<sub>3</sub>-monomer (**15**) to nonylnorbornene (**12**) ratios of 1:10, 1:20, and 1:50. The emission wavelength is observed to be blue-shifted with

15

decreasing chromophore density. Similar results can also be seen in Figure 7 for the **CHO**-polymer and Figure 8 for the **PVK**-polymer. While the shifts are different for each polymer, the trend is the same in all cases. However, a 1:100 ratio of **15:12** of the **CHO**-polymer showed identical emission peaks as that of the 1:50 **CHO**-polymer, therefore, this chromophore dilution effect appeared to be limited. While not intending to be bound by theory, this observation suggested that the emission wavelength is dependant on the packing of the AlqX<sub>2</sub>-complex, which is consistent with the notion that the shorter the inter-ligand contacts, the more red-shifted the emission. (See, Brinkmann, M.; Gadret, G.; Muccini, M.; Taliani, C.; Masciocchi, N.; Sirani, A. *J. Am. Chem. Soc.* **2000**, *122*, 5147-5157, which is incorporated by reference herein in its entirety.)

The effect of molecular weight on the optical properties was also investigated. As shown in Table 5, it was found that the changes in molecular weight have very little effect on the emission of the polymer, both in solution and the solid-state.

Figure 9 provides examples of catalysts that can be used for polymerizing the functionalized monomers to the functionalized polymers, based on a ring-opening metathesis polymerization (ROMP) catalytic process.

## 20 Fluorescence Studies on Znq<sub>2</sub> Complexes

All zinc-containing copolymers **18** were characterized using NMR, UV/Vis, and fluorescence spectroscopy, with the results being summarized in Table 8. The molecular weights of the copolymers ranged from about 8,000 to about 40,000, with polydispersities from about 1.5 and about 2.5 as determined by GPC. The UV/Vis and fluorescence spectra were recorded in dry chloroform. Figure 10 illustrates the solution fluorescence spectra of all Znq<sub>2</sub>-functionalized copolymers, excited at 380 nm, except for the **Naph** copolymer which was excited at 330 nm. Figure 11 demonstrates that the emission of the Znq<sub>2</sub>-functionalized copolymers can be tuned in solution from blue (427 nm) to the yellow (565 nm) through modifications on the second functionalized quinoline.

These results further demonstrate that the fluorescence properties of the material can be tuned in solution and that the polymer backbone does not interfere with the optical properties of the Znq<sub>2</sub> moiety.

The relative quantum yields of the zinc-containing copolymers **18** were calculated based on Alq<sub>3</sub> as the standard and are summarized in Table 8. Znq<sub>2</sub>-containing monomer was observed to have a higher quantum yield than Alq<sub>3</sub>. The 1:1, 1:5, and 1:10 Znq<sub>2</sub>-copolymers were observed to exhibit even higher quantum yields than their small molecule counterpart. It is not until the concentration of the Znq<sub>2</sub>-monomer dropped below about 10 mol% of the copolymer that the quantum yields decrease below that of Znq<sub>2</sub>. While not intending to be bound by theory, the increase in quantum yields going from Znq<sub>2</sub> to the 1:1 Znq<sub>2</sub>-copolymer to the 1:5 Znq<sub>2</sub>-copolymer indicates the possibility of some self-quenching occurring at higher Znq<sub>2</sub> concentrations.

**Table 8.** Photoluminescence and related data for Znq<sub>2</sub>-containing monomers and polymers.

Compound	Absorption $\lambda_{max}$	Solution Emission $\lambda_{max}$	Solid State Emission $\lambda_{max}$	Relative Quantum Yields
Alq <sub>3</sub>	381	525	519 <sup>a</sup>	1.0
Znq <sub>2</sub>	379	542	542 <sup>a</sup>	1.3
1:1 Znq <sub>2</sub>	378	544	548	1.0
1:5 Znq <sub>2</sub>	374	543	520	3.9
1:10 Znq <sub>2</sub>	375	545	512	2.0
1:20 Znq <sub>2</sub>	378	546	505	0.30
CHO	381	503	487	2.2
PVK	373	565	545	0.33
Naph	325	427	445	0.37
Quinox	379	510	467	0.44

<sup>a</sup> Reported in T. A. Hopkins, K. Meerholz, S. Shaheen, M. L. Anderson, A. Schmidt, B. Kippelen, A. B. Padias, J. H.K. Hall, N. Peyghambarian and N. R. Armstrong, *Chem. Mater.* 1996, **8**, 344; which is incorporated herein by reference in its entirety.

To characterize the solid-state properties of all Znq<sub>2</sub>-containing copolymers, thin films were spun on quartz slides, with thicknesses ranging between 200-400 nm as determined by ellipsometry. The fluorescence spectra were recorded at an excitation wavelength of 380 nm (**Naph** at 330 nm) and are shown in Figure 11, with the  $\lambda_{\text{max}}$  reported in Table 8. Similar to the solution studies, the emission colors of the films range from the blue to the yellow. The influence of the lumophore density on the solid-state properties was also investigated. The 1:1 copolymer emission, a high lumophore concentration, is red-shifted in comparison to the emission of the 1:20 copolymer. Regardless of the lumophore concentration and the quinoline ligand used, the emission of the thin films again indicated that the polymer backbone does not inhibit fluorescence, even in the solid-state. Conductivity of the films was measured using a four-point probe and resulted in conductivities ranging from 12 S/cm for the 1:1 Znq<sub>2</sub>-copolymer to 3.6 S/cm for the 1:20 Znq<sub>2</sub>-copolymers. The results obtained from these experiments suggested that the Znq<sub>2</sub>-polymers were able to support a current, which indicates these materials are useful in electroluminescent devices.

### *Definitions*

In order to more clearly define the terms used herein, the following definitions are provided. To the extent that any definition or usage provided by any document incorporated herein by reference conflicts with the definition or usage provided herein, the definition or usage provided herein controls.

As used herein, the terms Mq<sub>n</sub>-moiety, Mq<sub>n</sub>-containing moiety, and the like refer to a chemical moiety which comprises an Mq<sub>n</sub> residue, an Mq<sub>n</sub>-like residue, a functionalized Mq<sub>n</sub> residue, a functionalized Mq<sub>n</sub>-like residue, or similar structures. Thus, Mq<sub>n</sub>-moieties constitute that portion of the Mq<sub>n</sub>-functionalized molecule, monomer, or polymer that includes the Mq<sub>n</sub> core group, regardless of the functionalization of the 8-hydroxyquinoline ligands and regardless of the heteroatom substitutions within the 8-hydroxyquinoline ligands.

The term 8-hydroxyquinoline residue is used to refer to, among other things, an 8-hydroxyquinoline ligand that can be non-functionalized; functionalized with at least one electron-donating group, at least one electron-withdrawing group, or a combination thereof; can be deprotonated; can be partially hydrogenated; and the like; or any combination of these. In the usual sense, the 8-hydroxyquinoline residue of this invention comprises a deprotonated 8-hydroxyquinoline, therefore  $Mq_n$ -containing monomers and polymers refer to metal (M) complexes in the  $n^+$  oxidation state. This term is also used to refer to 8-hydroxyquinoline-like ligands such as, for example, ligands in which either another heteroatom is present in one of the 6-membered rings of the 8-hydroxyquinoline ligand, or a partially hydrogenated 8-hydroxyquinoline-like ligand. Examples of this type 8-hydroxyquinoline residue include, but are not limited to, the Naph and Quinox (also termed Quix) ligands illustrated in Figure 3. This term also refers to 8-hydroxyquinoline ligands, or their heteroatom substituted analogs, that can be functionalized with at least one group independently selected from: a hydrocarbonyl group, an oxygen group, a sulfur group, a nitrogen group, a phosphorus group, an arsenic group, a carbon group, a silicon group, a germanium group, a tin group, a lead group, a boron group, an aluminum group, an inorganic group, an organometallic group, or a substituted analog thereof, any one of which having from 1 to about 30 carbon atoms; a halide; hydrogen; or any combination thereof.

The terms polymerizable moiety, polymerizable unit, polymerizable residue, and the like refer to a chemical moiety containing a polymerizable functional group. Examples of polymerizable functional groups include, but are not limited to, alkenes, alkynes, butadienes, and the like, although viable polymerizable functional groups depending upon factors that include, but are not limited to, the polymerization method, polymerization catalyst, monomer containing that polymerizable functional group, and the like. Examples of polymerizable moieties, units, residues, and the like, include, but are not limited

to norbornene, norbornadiene, cyclopentene, cyclooctene, cyclooctadiene, or functionalized analogs thereof.

## EXAMPLES

5           The present invention is further illustrated by the following examples, which are not to be construed in any way as imposing limitations upon the scope thereof. On the contrary, it is to be clearly understood that resort may be had to various other embodiments, modifications, and equivalents thereof which, after reading the description herein, may suggest themselves to one of ordinary skill in  
10   the art without departing from the spirit of the present invention or the scope of the appended claims.

### EXAMPLE 1

#### *General Synthetic and Characterization Details*

15           Unless otherwise specified, all chemicals were purchased from Acros Organics or Aldrich and used without further purification. All reactions were performed in atmospheric conditions unless otherwise noted. Flash column chromatography was carried out on silica gel 60, 230-400 mesh (Whatman or Sorbent Tech). The  $^1\text{H}$  ( $^{13}\text{C}$ ) NMR spectra were recorded at 300 (75) MHz on a  
20   Varian Mercury 300 spectrometer. Chemical shifts are reported in ppm on the  $\delta$  scale relative to the solvent residual proton signal. Mass spectra were obtained on a Micromass Quattro LC spectrometer or a VG-70se spectrometer. Elemental analyses were performed on a Perkin-Elmer CHNS/O Analyzer Series II 2400.

          Differential scanning calorimetry (DSC) was performed under nitrogen  
25   using either a Perkin-Elmer DSC 7 equipped with an Intracooler II device, wherein the temperature program provided heating and cooling cycles between 0°C and 300°C at 20°C/min, or provided heating and cooling cycles between -30°C and 150°C at 10 °C/min. Differential scanning calorimetry (DSC) was also performed under nitrogen using a Netzsch STA 409 PG DSC coupled with a  
30   Netzsch TG 209 thermal gravimetric analyzer, wherein the temperature program

provided a heating rate of 20°C/min from room temperature up to 800°C. Thermogravimetric analysis (TGA) measurements were also performed using Netzsch TG 209 from 30 to 800 °C at 20 °C/min.

For some samples, gel permeation chromatography (GPC) analyses were carried out using a Waters 1525 binary pump coupled to a Waters 2414 refractive index detector. The GPC was calibrated using polystyrene standards on a Styragel® HR 4 and HR 5E column set with CH<sub>2</sub>Cl<sub>2</sub> as an eluent. For other samples, gel permeation chromatography (GPC) analyses were carried out using a Waters 1525 binary pump coupled to a Waters 410 refractive index detector. The GPC was calibrated using polystyrene standards on an American Polymer Standards 10μ particle size, linear mixed bed packing columns set with CH<sub>2</sub>Cl<sub>2</sub> as an eluent.

The UV/Visible spectra were obtained on a Perkin-Elmer Lambda 19 UV/VIS/NIR Spectrometer. The fluorescence spectra were obtained on a Spex Fluorolog Spectrofluorometer. Ellipsometry measurements were taken on a J. A. Woollam Co. Inc. Spectroscopic Ellipsometer, M-2000VI.

Compounds **1-3** and **6** were synthesized from the following literature procedures: Clemo, G. R.; Howe, R. *J. Chem. Soc.* **1955**, 3552-3553; Giraudi, G.; Baggiani, C.; Giovannoli, C.; Marletto, C.; Vanni, A. *Anal. Chim. Acta* **1999**, 378, 225-233; and Stubbs, L. P.; Weck, M. *Chem. Eur. J.* **2003**, 9, 992-999; each of which is incorporated herein by reference in its entirety.

The modified 8-hydroxyquinoline ligands abbreviated as **Naph**, **Quinox**, **Ph**, **CHO**, and **PVK** were prepared from literature procedures, as described in: Meyers, A.; Weck, M. *Macromolecules* **2003**, 36, 1766-1768; Freeman, S. K.; Spoerri, P. E. *J. Org. Chem.* **1951**, 16, 438-442; Eck, T. D.; Wehry Jr., E. L.; Hercules, D. M. *J. Inorg. Nucl. Chem.* **1966**, 28, 2439-2441; Hojjatie, M.; Muralidhara, S.; Dietz, M. L.; Freiser, H. *Synth. Comm.* **1989**, 19, 2273-2282; and Clemo, G. R.; Howe, R. *J. Chem. Soc.* **1955**, 3552-3553; each of which is

incorporated herein by reference in its entirety. The remaining modified 8-hydroxyquinoline ligands used in this invention were commercially available.

## EXAMPLE 2

### 5 *Preparation of 6-Bicyclo[2.2.1]hept-5-en-2-yl-hexylamine (4)*

A solution of the nitrile **3** (1.052 g, 0.005 mol) in diethyl ether was added dropwise to a LiAlH<sub>4</sub> suspension (0.43 g, 0.011 mol in 40 mL diethyl ether) at 0 °C. The mixture was allowed to warm to room temperature over a period of an hour, refluxed for 30 minutes, and then cooled back to room temperature. Water  
10 was added to neutralize any excess LiAlH<sub>4</sub>. The ether layer was washed with water, 20% NaOH, brine, and dried over Na<sub>2</sub>SO<sub>4</sub>. The ether was removed to give a pale yellow liquid, which needed no further purification (0.726 g 67%). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 6.07 (1H endo, dd, *J* = 2.74, 5.49); 6.03-5.97 (2H exo, m); 5.87 (1H endo, *J* = 2.74, 5.49); 2.70 (2H, s); 2.65 (2H, t, *J* = 7.14); 1.94-1.74  
15 (2H, m); 1.43-0.99 (12H, m); 0.46-0.40 (1H, m). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 137.1; 132.6; 49.8; 45.6; 42.7; 42.4; 38.9; 34.9; 33.9; 32.6; 29.9; 28.8; 27.1. HRMS (EI): calcd for C<sub>13</sub>H<sub>23</sub>N<sub>1</sub> [M]<sup>+</sup>. 193.1832, found 193.1852.

## EXAMPLE 3

### 20 *Preparation of 5-[(6-Bicyclo[2.2.1]hept-5-en-2-yl-hexylimino)-methyl]-quinolin-8-ol (7)*

Amine **4** (0.726 g, 0.00376 mol) and 5-formyl-8-hydroxyquinoline **6** (0.650 g, 0.00376 mol) were dissolved in 40 mL of benzene and refluxed for 18 hours. After cooling, the solvent was removed under reduced pressure to yield  
25 the product as an orange solid (1.308 g, 100%). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 9.75 (1H, dd *J* = 8.79, 1.64); 8.81 (1H, dd, *J* = 1.64, 4.39); 8.59 (1H, s); 7.69 (1H, d, *J* = 8.24); 7.56 (1H, dd, *J* = 4.39, 8.79); 7.19 (1H, d, *J* = 7.69); 6.10 (1H endo, dd, *J* = 2.74, 5.49); 6.06-5.99 (2H exo, m); 5.91 (1H endo, dd, *J* = 2.74, 5.94); 3.67 (2H, t, *J* = 7.14); 2.74 (2H, s); 1.99-1.69 (4H, m); 1.42-1.01 (12H, m); 0.50-0.44



(1H, m). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 160.8; 154.2; 148.1; 138.4; 137.0; 135.3; 133.0; 132.6; 127.0; 123.3; 123.2; 109.2; 62.9; 49.7; 45.6; 42.7; 38.9; 34.9; 32.6; 31.4; 29.9; 28.8; 27.6. HRMS (EI): calcd for C<sub>23</sub>H<sub>28</sub>N<sub>2</sub>O<sub>1</sub> [M]<sup>+</sup> 348.2201, found 348.2186.

5

#### EXAMPLE 4

##### *Preparation of 5-[(6-Bicyclo[2.2.1]hept-5-en-2-yl-hexylamino)-methyl]-quinolin-8-ol (8)*

Imine 7 was dissolved in 50 mL of dry methanol and 1 equivalent of  
10 NaBH<sub>4</sub> (0.136 g, 0.0036 mol) was added in small increments. After the addition was complete, the solution was allowed to stir for 10 minutes at room temperature. The solution was diluted with water and extracted three times with 20 mL of methylene chloride. The combined organic layers were washed with water, NaHCO<sub>3</sub>, brine, and dried over Na<sub>2</sub>SO<sub>4</sub>. The solvent was removed under  
15 reduced pressure to yield a brown liquid. Purification by column chromatography (silica gel, 4:1 hexanes/ethyl acetate, then pure ethyl acetate, then 5% methanol in ethyl acetate) gave the product as a pale yellow solid (0.658 g, 50%). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 8.75 (1H, dd, *J* = 1.09, 4.39); 8.51 (1H, dd, *J* = 1.09, 8.24); 7.46 (1H, dd, *J* = 4.39, 8.24); 7.38 (1H, d, *J* = 7.69); 7.08 (1H, d, *J* = 7.69); 6.11  
20 (1H endo, dd, *J* = 2.74, 5.49); 6.06-5.99 (2H exo, m); 5.90 (1H endo, dd, *J* = 2.74, 5.49); 4.10 (1H, s); 2.73 (2H, s); 2.71 (2H, t, *J* = 7.14); 1.99-1.02 (12H, m); 0.49-0.43 (1H, m). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 151.8; 147.6; 137.0; 136.3; 133.4; 132.6; 128.0; 127.4; 126.8; 121.8; 109.2; 51.2; 50.0; 49.7; 45.5; 42.7; 38.9; 34.9; 32.6; 30.2; 29.9; 28.8; 27.5. Anal. Calcd for C<sub>23</sub>H<sub>30</sub>N<sub>2</sub>O: C, 78.88; H, 8.63;  
25 N, 8.00. Found C: 78.79, H: 8.72, N: 8.00.

#### EXAMPLE 5

##### *Preparation of the Alq<sub>3</sub>-functionalized monomer 9*

The formation of the Alq<sub>3</sub>-functionalized monomer 9 was achieved by  
30 adding monomer 8, dissolved in 10 mL of dry THF, dropwise to ten equivalents

of triethylaluminum, dissolved in 10 mL of dry THF, and stirring under argon for 2 hours. Then 20 equivalents of 8-hydroxyquinoline, dissolved in 10 mL THF was added dropwise to the monomer solution, and the solution was stirred overnight under argon. Any precipitate that formed was filtered off and the solvent was removed to yield a bright yellow solid. This product was used without further purification in the polymerization procedure.

### EXAMPLE 6

#### *Preparation of 5-Nonyl-bicyclo[2.2.1]hept-2-ene (12)*

10 An oven-dried 3-neck round bottom flask was charged with magnesium turnings (0.809 g, 0.033 mol) and 40 mL of dry THF. 5-Bromomethylnorbornene (6.001 g, 0.032 mol) was added dropwise at room temperature. The mixture was then heated to 50 °C for 18 hours. In a separate flask, 10 mL of dry THF,  $\text{Li}_2\text{CuCl}_4$  (5 mL, 0.0005 mol), and 1-bromooctane (6 mL, 0.035 mol) were  
15 combined and placed in a -10 °C ice bath. The Grignard reagent, which was transferred via cannula into an addition funnel, was added dropwise to the cooled solution. After the addition was complete, the solution was warmed to room temperature and stirred for 18 hours. The solution was diluted with ether, washed with  $\text{NH}_4\text{Cl}$ , brine, and dried over  $\text{Na}_2\text{SO}_4$ . The solvent was removed and the  
20 product was distilled at 76 °C at 0.4 mbar to yield a clear, colorless liquid (4.88 g, 69%).  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  6.12 (1H endo, dd,  $J = 2.74, 5.49$ ); 6.09-5.99 (2H exo; m); 5.93 (1H endo, dd,  $J = 2.74, 5.49$ ); 2.75 (1H, s); 1.98-1.78 (2H, m); 1.40-1.07 (18H, m); 0.89 (3H, t,  $J = 6.05$ ); 0.52-0.45 (1H, m).  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  137.0; 132.6; 49.7; 45.6; 42.7; 38.9; 35.0; 32.6; 32.1; 30.1; 29.9;  
25 29.8; 29.5; 28.9; 22.9; 14.3.

## EXAMPLE 7

*Preparation of 5-[6-Bicyclo[2.2.1]hept-5-en-2-yl-hexylamino)-methyl]-8-quinolinato-(dihydroxy)-aluminum (14).*

The monomer 5-[(6-Bicyclo[2.2.1]hept-5-en-2-yl-hexylamino)-methyl]-quinolin-8-ol (**8**) (0.025 g, 0.07 mmol) was dissolved in 5 mL benzene, and added dropwise to a solution of triethylaluminum (0.04 mL, 0.07 mmol) in 10 mL benzene, Scheme 5. The reaction was stirred for 2 hours under argon, the precipitate was filtered off, and the solvent was removed to yield a yellow solid **14** (0.03 g, 96% yield). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 8.86 (0.5H, dd, *J*<sub>I</sub> = 4.94, 17.58); 8.68 (0.5H, m); 7.72 (1H, dd, *J* = 3.29, 5.50); 7.54 (2H, m); 7.03 (1H, t, *J* = 8.24); 6.11 (1H endo, dd, *J* = 2.74, 5.49); 6.06-5.99 (2H exo, m); 5.90 (1H endo, dd, *J* = 2.74, 5.49); 4.10 (1H, s); 2.73 (2H, s); 2.71 (2H, t, *J* = 7.14); 1.99-1.02 (12H, m); 0.49-0.43 (1H, m). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 137.0; 132.8; 51.2; 50.0; 49.7; 45.5; 42.7; 38.9; 34.9; 32.6; 30.2; 29.9; 28.8; 27.5.

## EXAMPLE 8

*Preparation of 5-[6-Bicyclo[2.2.1]hept-5-en-2-yl-hexylamino)-methyl]-8-quinolinato-(diligand X)-aluminum (15a-15j)*

Two equivalents of a modified 8-hydroxyquinoline ligand **X**, examples of which are shown in Figure 3 and which are abbreviated as **X** in Scheme 5, were dissolved in benzene and added dropwise to one equivalent of the dihydroxy monomer **14**, dissolved in 10 mL of benzene. The solution was allowed to stir under argon for two hours, followed by the removal of the solvent to yield a solid ranging in color from bright yellow to dark orange. The exceptions to this procedure are when **X** was 4-hydroxy-1,5-naphthyridine (**Naph**) or 8-hydroxyquinoline-5-sulfonic acid. (**SO<sub>3</sub>H**) These compounds were dissolved in DMSO, while monomer **14** was dissolved in THF.

The resulting functionalized Alq<sub>3</sub>-containing monomers provided by this procedure are shown in Table 1.

## EXAMPLE 9

### *General Polymerization Procedure*

Monomers **9**, **15** (**15a-15j**), and **12**, as needed, were dissolved in chloroform in the desired ratio, the ruthenium catalyst **11** was dissolved in chloroform, and both solutions were combined. The polymerizations were monitored by NMR and were complete within 12 hours. All polymers were purified by repeated precipitation into methanol. Again, the exceptions to this procedure are when the functionalized monomer **X** was 4-hydroxy-1,5-naphthyridine or the 8-hydroxyquinoline-5-sulfonic acid. In these cases, the AlqX<sub>2</sub>-monomer **Naph** and **SO<sub>3</sub>H** were dissolved in a 1:1 ratio of DMSO/chloroform.

## EXAMPLE 10

### *Solution Photoluminescence Studies*

Approximately 5 mg of each of the polymers shown in Table 5 was dissolved in 10 mL of chloroform. Dilutions were made as needed. UV/Visible and fluorescence measurements were taken in a 1.0 cm quartz cell.

## EXAMPLE 11

### *Thin Film Fabrication and Characterization*

The concentrations of the polymers in solution were varied from 15-100 mg of polymer per mL of chloroform. One drop of each solution was dropped onto a quartz slide spinning at 2000 rpm. The polymer solutions that showed the highest fluorescence intensity in the solid-state ranged from 30-50 mg/mL. The films made for the ellipsometry experiment were prepared in a similar manner using gold-coated glass slides (100 nm of Au) instead of quartz slides. The film thicknesses were measured by ellipsometry by collecting data every 5° from 65° to 75° and were fitted using a Cauchy film on gold model. The resistances of the films were measured using a Keithley 196 system and an Ai alessi four-point probe. The probe was lowered until it came in contact with the surface of the

films and the resistance was recorded. Conductivity was determined based on the equation:  $\sigma = 0.221 (R \cdot t)^{-1}$ , where R is the resistance in ohms, t is the thickness of the film in centimeters, and  $\sigma$  is the conductivity in Siemens/cm. (See: Smits, F.M. *Bell Syst. Tech. J.* **1958**, 710-718.)

5

#### EXAMPLE 12

##### *Spin-Casting Procedure*

The copolymers prepared according to this invention were dissolved in chloroform at a concentration of approximately 30 mg/mL. Using a Specialty  
10 Coating Systems P-6000 spin coater, the solution was dropped onto an ITO-coated glass slide, spinning at 1200 rpm.

#### EXAMPLE 13

*Preparation of 5-[6-Bicyclo[2.2.1]hept-5-en-2-yl-hexylamino)-methyl]-8-quinolinato-(ligand X)-zinc (2).*  
15

Monomer 8 (0.025 g, 0.07 mmol) was dissolved in 5 mL dry benzene and added dropwise to a solution of diethylzinc (0.04 mL, 0.07 mmol) in 10 mL dry benzene. The reaction was stirred for two hours under argon. The resulting precipitate was filtered off and the solvent was removed to yield a yellow solid  
20 which was used without further purification (0.03 g, 96 % yield). One equivalent of the modified 8-hydroxyquinoline ligands X was dissolved in 10 mL dry benzene and added dropwise to one equivalent of the zinc-monomer, dissolved in 10 mL of dry benzene. The solution was allowed to stir under argon for two hours, followed by the removal of the solvent to yield a solid ranging in color  
25 from bright yellow to dark orange.

#### EXAMPLE 14

##### *Thin Film Fabrication and Characterization of Znq<sub>2</sub>-Copolymers*

The concentrations of the Znq<sub>2</sub>-containing polymers in solution were  
30 varied from 15-100 mg of polymer per mL of dry chloroform. One drop of each

solution was dropped onto a quartz slide spinning at 2000 rpm. The polymer solutions that showed the highest fluorescence intensity in the solid-state ranged from 30-50 mg/mL. The films made for the ellipsometry experiment were prepared in a similar manner using gold-coated glass slides (100 nm of Au) instead of quartz slides. The film thicknesses were measured by ellipsometry by collecting data every 5° from 65° to 75° and were fitted using a Cauchy film on gold model. The resistances of the films were measured using a Keithley 196 system and an Ai alessi four-point probe. The probe was lowered until it came in contact with the surface of the films and the resistance was recorded.

Conductivity was determined based on the equation:  $\sigma = 0.221 (R \cdot t)^{-1}$ , where R is the resistance in ohms, t is the thickness of the film in centimeters, and  $\sigma$  is the conductivity in Siemens/cm<sup>2</sup>.